THESIS

STABLE ISOTOPE (δ^2H AND $\delta^{18}O$) CHARACTERIZATION OF THE SOUTH PLATTE RIVER, COLORADO

Submitted by

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ABSTRACT

STABLE ISOTOPE (δ^2H AND $\delta^{18}O$) CHARACTERIZATION

OF THE SOUTH PLATTE RIVER, COLORADO

Stable isotope compositions (δ^2H and $\delta^{18}O$) were examined at 13 sites along the South Platte River, Colorado during the water year 2009-2010. As a natural part of the water molecule, stable isotope (δ^2H and $\delta^{18}O$) compositions are used as indicators to trace flow of water in the hydrologic cycle, allowing the identification of sources of water and evaporation processes. A strong positive correlation was determined between δ^2H and $\delta^{18}O$ compositions along the South Platte River, from Henderson to Julesburg, CO. All isotope compositions plotted below the global and regional meteoric water lines, indicating these were enriched in the heavy isotope forms relative to precipitation. Isotopic compositions were observed to vary spatially and temporally and between low and high flows. Mean isotope compositions became enriched with distance downstream from Henderson (-110.2 ‰ δ^2H and -14.4 ‰ $\delta^{18}O$) to Julesburg (-94.5 ‰ δ^2H and -12.0 ‰ $\delta^{18}O$). Mean isotope compositions also varied during different seasonal periods, with enriched compositions in the fall (September and October) (-98.9 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$) and winter (January and February) (-100.7 ‰ δ^2H and -12.5 ‰$\delta^{18}O$) seasons of 2009-2010 relative to those during the summer (June and July) (-104.8 ‰ δ^2H and -13.5

‰ $\delta^{18}O$) of 2009 and the spring (April and May) (-102.8 ‰ $\delta^{2}H$ and -13.6 ‰ $\delta^{18}O$) and summer (June) (-114.1 ‰ $\delta^{2}H$ and -15.2 ‰ $\delta^{18}O$) seasons of 2010. Furthermore, mean stable isotope compositions were generally enriched during the low flow (-99.5 ‰ $\delta^{2}H$ and -12.8 ‰ $\delta^{18}O$) period from July 2009 to April 2010 relative to the high flow (-110.1 ‰ $\delta^{2}H$ and -14.3 ‰ $\delta^{18}O$) period in June 2009, May and June 2010. The observed enrichment and changes in isotope compositions could have been due to: 1) the contribution to river discharge of different sources of water characterized by particular isotope signatures 2) evaporation processes where lighter isotope forms are favorably transformed to the vapor phase, concentrating the heavier isotope forms in the liquid phase 3) a change of origin of vapor sources with varying isotope signatures during different seasons and 4) a combination of the above.

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INTRODUCTION

In arid regions, precipitation and evaporation are natural processes that directly affect the availability of surface water resources. For a semi-arid river, such as the South Platte River (SPR) in Colorado, hydrologic cycle processes like precipitation, evaporation, snowmelt and groundwater partly control flow variations in the river. Wastewater discharge and storage reservoirs affect flow as well. The SPR was characterized by low to nonexistent water levels during the summer and high flow levels during the spring due to snowmelt in the headwaters [Camp Dresser and McKee, 1994]. With increasing human populations, the demand created for water resources by industrial, municipal and agricultural purposes led to the development of methods that control and regulate river flow through wet seasons to supply water for these demands during dry periods [Saunders III and Lewis Jr., 2003]. The SPR is a highly controlled system where reservoirs, other storage structures and trans-basin water transport regulate river flows to supply water for the generated demands [Camp Dresser and McKee, 1994].

The stable isotopes of ^{2}H and ^{18}O occur naturally as part of the water molecule and have been utilized as tracers to provide information on physical, kinetic and chemical processes that affect water molecules as they are transported through the different stages of the hydrologic cycle [Bowen, 1986; Kendall and McDonnell, 1998; Aggarwal et al., 2005; Singh and Kumar, 2005]. As a tracer, isotopic compositions of water have been used as a method of characterizing and quantifying the effect of different flow contributing sources to a river system and the effect evaporation processes cause in discharge and water quality of a stream [Simpson and Herczeg, 199; Kattan, 2007]. In this study, stable isotope compositions of the South Platte River were measured to explore how evaporation, the different contributing sources of water to the river and the different flow periods of the river affect the stable isotope compositions of water in this controlled semi-arid river system.

1.1 Stable Isotopes of Water

Hydrogen occurs naturally as three isotopes; ^{1}H, ^{2}H (deuterium) and ^{3}H (tritium), and oxygen has three isotopes; ^{16}O, ^{17}O and ^{18}O. Every form of both hydrogen and oxygen isotopes are present in the Earth in different quantities of which the average percentages found in nature are approximately 99.985%, 0.015% and 10^{-15} % for hydrogen isotopes ^{1}H, ^{2}H and ^{3}H, respectively, and 99.759%, 0.037% and 0.204% for oxygen isotopes ^{16}O, ^{17}O and ^{18}O, respectively [Bowen, 1986; Harris, 2005]. Water molecules with different hydrogen and oxygen compositions are formed due to the existence and availability of the different isotopes. The four main isotopic combinations forming water molecule compounds found in nature are $^{1}H_{2}{}^{16}O$, $^{1}H^{2}H^{16}O$, $^{1}H_{2}{}^{18}O$ and

$^{1}H^{3}H^{16}O$ [Araguas-Araguas et al., 1997; Singh and Kumar, 2005]. The transformation of water between gas, liquid and solid phases fractionates the isotopic components of water molecules producing variations in the ^{2}H and ^{18}O isotopic compositions of water molecules in any body of water [Singh and Kumar, 2005] (Figure 1). Fractionation processes are dependent on mass differences of isotopes, which determine the composition of every individual water molecule [Kendall and McDonnell, 1998]. Assuming isotopic signatures of sources of water do not change during the mixing process, the contribution of each source to a river system may be determined by the isotopic composition of stable isotopes of hydrogen and oxygen in the mixture [Clark and Fritz, 1997; Liu et al., 2008].

With this assumption, isotopic compositions of water molecules have been utilized as tracers in watershed systems [Clark and Fritz, 1997] providing information in the determination of water age, mixing between different waters [Bowen, 1986], the description of flow paths generated by precipitation to discharge at a stream, detection of contaminant sources for different solutes [Litke, 1994-95; Kendall and McDonnell, 1998], determination of flow velocity and direction [Singh and Kumar, 2005] and in the determination of water sources (e.g., groundwater, soil water content) for plants and crops within seasonal periods [McCole and Stern, 2007].

Tracing the movement and isotopic composition variations of water molecules in a semi-arid system like the SPR, might signal the main sources (e.g., snowmelt, treated wastewater, groundwater) contributing to river discharge, as these sources of water are

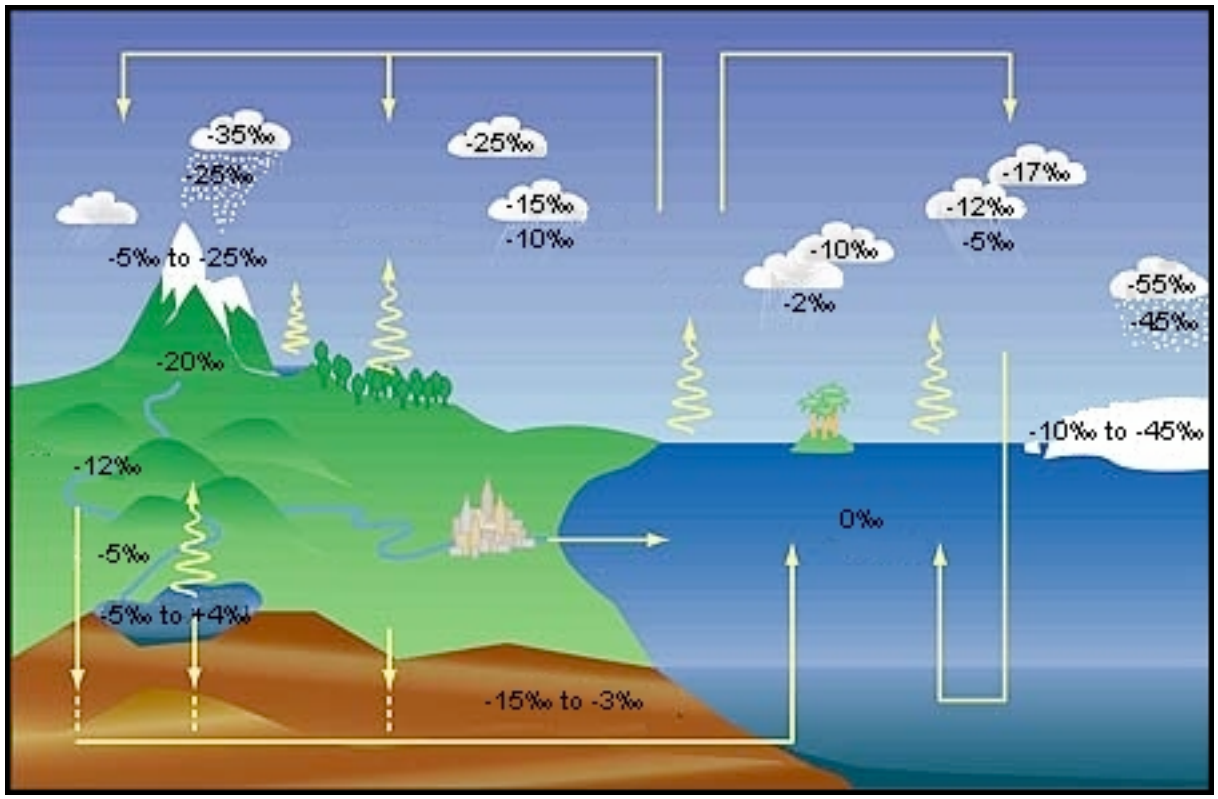

Figure 1. Isotope Compositions in the Hydrologic Cycle. Isotopic compositions of hydrogen and oxygen are partitioned differently under equilibrium and non-equilibrium conditions within the components of the hydrologic cycle. Illustrated is the change in isotope compositions of ^{18}O through the hydrologic cycle. [http://atoc.colorado.edu: adapted from GNIP Brochure, IAEA, 1996].

characterized by distinct isotopic compositions. This technique has been tested and proved in studies conducted worldwide [e.g., Payne et al., 1979; Simpson and Herczeg, 1991; Coplen et al., 2000; Winston and Criss, 2003; Kattan, 2007; Lee and Kim, 2007; Liu et al., 2008].

1.2 Isotopic Compositions in the Hydrologic Cycle

The isotopic compositions of the components of the hydrologic cycle are unique to specific climatic zones, like evaporation from ocean water, precipitation, snow, ice accumulation, melting and runoff [Clark and Fritz, 1997]. The characteristic isotopic compositions for each of these hydrologic cycle components can be used to trace and identify contributions of these to a surface water body.

1.2.1 Precipitation

Precipitation is a component of the hydrologic cycle where water condenses and produces rain, snow or hail that reach the land surface. Isotopic compositions of the parent cloud and the temperature at which condensation occurs determine the isotopic composition of precipitation [Kendall & McDonnell, 1998]. The isotopic compositions of each parent cloud that generates precipitation will vary depending directly on temperature, the distance the air mass has traveled from its source area, the change in altitude over topographic features, differences in latitude and seasonal variations [Clark and Fritz, 1997]. Generally, due to Rayleigh processes that occur while condensation takes place from the water vapor source, the heavier isotopes ^{2}H and ^{18}O become enriched in the liquid or solid phase and the lighter isotopes remain in the vapor phase

because mass differences will allow heavier isotope forms to precipitate first [Araguas-Araguas et al., 1997; Kendall and McDonnell, 1998].

Even though Rayleigh processes cause this enrichment-depletion tendency, altitude and seasonal variations affect the magnitude at which this behavior is observed. Isotope compositions in precipitation originating from the same water vapor source with the same isotope composition will vary in highlands and lowlands. As moisture is transported from a higher altitude to a lower one, more evaporation and re-evaporation processes take place, causing more enrichment in ^{2}H and ^{18}O compositions in the lowlands and more depleted compositions in the mountains [Bowen, 1986]. Isotope compositions vary with distance inland as the heavier isotope forms precipitate first, leaving the vapor enriched in the lighter isotope forms with increasing distance from the origin of the vapor source [Mazor, 2004]. Evaporation also occurs with seasonal changes, as precipitation is more susceptible to fractionation processes with the increase in temperature during the summer than during the winter [Kendall and McDonnell, 1998]. These isotope composition variations give an input signal characterized by Local Meteoric Water Lines particular to each region, thus permitting the tracing of recharge sources [Clark and Fritz, 1997].

1.2.2 Evaporation

Evaporation is a process of the hydrologic cycle in which liquid water is transformed to water vapor. As water molecules in the liquid phase are supplied with necessary heat energy (dependent on local temperature, humidity and wind), these are transformed into the vapor phase [Mazor, 2004]. When evaporation (vapor phase) occurs

from surface water (liquid phase), due to differences in vapor pressure, the isotopic compositions between these two phases are variable [Hoefs, 2004]. Mass differences present in isotopic compositions of water molecules allow the lighter isotopes of hydrogen and oxygen (^{1}H and ^{16}O) to evaporate faster than the heavier isotopes (^{2}H and ^{18}O), causing the water vapor to become enriched in the lighter isotope form and the residual water to become enriched in the heavier isotopes that are left behind [Mazor, 2004].

Evaporation generally occurs from a surface water body to the atmosphere but it might also take place during precipitation, triggering an isotopic exchange of the liquid or solid water (precipitation) and the atmospheric water vapor [Hoefs, 2004]. Because atmospheric water vapor has a differing isotopic composition than rain or snowfall, when evaporation occurs, the isotopic composition of precipitation will be enriched with decreasing elevation as the lighter isotope forms are evaporated first [Hoefs, 2004].

1.2.3 Snowmelt

During months of low temperatures, precipitation is received mainly as snow that is deposited on the land surface. As mentioned in section 1.1.1.1, fractionation processes that affect isotopic compositions occur between this solid phase and the water vapor as a result of different vapor pressures. With the freezing of water, snow will be enriched in the heavy isotopes of water ^{2}H and ^{18}O; due to mass differences, as snow forms, the heavier isotope forms will precipitate first [Clark and Fritz, 1997]. As freezing continues, the condensing water will have continuously depleted values of ^{2}H and ^{18}O because the amount of water molecules with the heavy isotope forms remaining in the air mass will

gradually decrease with time as these have precipitated first and will cause water molecules with the lighter isotope forms to condense [Clark and Fritz, 1997].

During snowmelt, liquid leaving the snowpack is depleted in the heavy isotopes of water with respect to the solid because the lighter forms of water have weaker bonds which are easier to break and thus will melt first leaving behind the stronger bonds formed by the heavier isotopes [Kendall and McDonnell, 1998]. Snowmelt usually has depleted $\delta^{2}H$ and $\delta^{18}O$ compositions relative to precipitation and groundwater, while isotopic variations between precipitation and groundwater are often hard to distinguish [Kendall and McDonnell, 1998]. In cold and high altitude regions, snowmelt and some rainfall may produce most of the streamflow during the melting period; during cold periods when snow is stored on the land surface, streams usually have low discharge because much of this precipitation is immobile and the groundwater levels start to decrease as less recharge is received and subsurface flow drains into the river or stream [Kendall and McDonnell, 1998]. When snowmelt occurs, higher discharge flows occur and groundwater levels are increased creating shorter flow paths for water to be transported through the subsurface to the river. The combined contributions of snowmelt (overland flow) and subsurface flow (groundwater and high water tables) might cause stream flow in a river system to reach its annual peak [Kendall and McDonnell, 1998].

1.2.4 Irrigation Return Flows

Irrigation return flows are water flows that are transported through the unsaturated zone generated by the infiltration of water used for irrigation. Transport of water through the unsaturated zone may be affected by the type of vegetation, non-saturated flow

through heterogeneous media, evaporation and transpiration losses and seasonal dependent recharge, which controls the percentage of infiltrating water that reaches the water table [Clark and Fritz, 1997]. Isotopic partitioning as a result of soil properties or chemical reactions occurring within geologic formations, recharge received from already partially evaporated surface water bodies and recharge received from precipitation that occurred during a past period having different isotopic compositions than those of present precipitation, may all cause variations that produce isotopic differences between precipitation and groundwater resources [Hoefs, 2004].

Irrigation water recharging the subsurface will be enriched in dissolved ions as a result of evapotranspiration, which might also cause enrichment of hydrogen and oxygen heavy isotopes and a higher concentration of fertilizers, pesticides and nitrate besides other pollutants [Mazor, 2004]. Transpiration is found to be a minimal to non-fractionating process of stable isotopes compared to evaporation, which might affect the isotopic compositions of water from the soil encountered within 20 meters of the surface [Kendall and McDonnell, 1998]. Evaporation processes taking place in the soil enriches the heavy isotopes ^{2}H and ^{18}O in the remaining water because the lighter isotope form will evaporate first [Kendall and McDonnell, 1998].

1.3 Global Meteoric Water Line

Isotopic compositions of ^{2}H and ^{18}O in water molecules are measured relative to the reference standard known as the Vienna Standard Mean Ocean Water (VSMOW), a mixture of distilled ocean water and smaller amounts of several other waters collected by the Scripps Institution of Oceanography, that serves as a global reference water sample

for isotope-ratio measurements [Aggarwal et al., 2005]. Isotopic compositions of water are measured by their ratios following the formula:

$$\delta = ({}^{2}H/{}^{1}H_{\text{sample}} - {}^{2}H/{}^{1}H_{\text{reference}})/{}^{2}H/{}^{1}H_{\text{reference}} \quad (1)$$

reported in a per mil basis (δ x 1000 = ‰), due to the small amount detected [Singh and Kumar, 2005]. The isotopic composition ratio in the measured water sample is positive δ when this value is higher than that of the standard and when this value is a negative δ it is lower than the standard [Kendall and McDonnell, 1998]. The isotopic composition values for VSMOW, serve as a zero point reference for the comparison of the isotopic compositions of other sources of water; meaning that when the δ value of a sample is higher than that of the VSMOW, the water sample is enriched in that isotope form ($\delta^{2}H$ and $\delta^{18}O$) relative to the reference material and when the δ is lower than the reference material, the isotope compositions of the sample is depleted relative to that of the VSMOW [Aggarwal et al., 2005]. Isotope compositions of a water sample x are enriched relative to those of another water sample y when the amount of ^{2}H and ^{18}O is higher (less negative) in the water sample x and vice versa. If a water sample x has a smaller amount (more negative) of ^{2}H and ^{18}O relative to a water sample y, then the water sample x is said to be depleted relative to water sample y.

After analyzing isotopic compositions of water samples from rain, snow and diverse surface water bodies worldwide, a linear relationship between the isotope forms $\delta^{2}H$ and $\delta^{18}O$ compositions in natural water derived from precipitation was identified and is known as the Global Meteoric Water Line (GMWL); $\delta^{2}H = 8\delta^{18}O + 10‰$ [Craig,

1961] (Figure 2). From the δ^2H-$\delta^{18}O$ relationship described by the GMWL, the deuterium-excess parameter is defined as $d = \delta^2H - 8\delta^{18}O$ [Bowen, 1986; Aggarwal et al., 2005]. Isotopes of ^2H are also reported as δ Deuterium (δD). The ratio of heavy to light isotope forms while water vapor is formed from the ocean under non-equilibrium conditions, yields a slope of 8 for the GMWL [Aggarwal et al., 2005]. The deuterium excess parameter is a factor describing isotope fractionation occurring under close-to equilibrium conditions from the change of atmospheric vapor to the liquid phase [Kendall and McDonnell, 1998; Aggarwal et al., 2005]. The deuterium excess value of 10 ‰ in the Global Meteoric Water Line is based on global atmospheric water vapor that forms at a humidity of approximately 85%, producing a precipitation line shifted from the seawater line by 10‰ [Clark and Fritz, 1997].

1.3.1 Rayleigh Processes

Isotope fractionation that occurs during evaporation-condensation processes in the air column is described by a series of equations that define patterns and ratios at which isotope compositions fractionate under equilibrium conditions between the vapor and liquid phases [Rayleigh, 1986]. Condensation processes that form meteoric waters occur under equilibrium and a humidity of 100%, which sets the slope of the GMWL to be approximately 8 [Kendall and McDonnell, 1998; Singh and Kumar, 2005]. For condensation processes that occur under non-equilibrium conditions, the isotope compositions of water will fractionate differently which will be indicated by isotope ratios that are enriched or depleted with respect to ^2H and ^{18}O [Rayleigh, 1986; Araguas-Araguas et al., 2000; Hoefs, 2004].

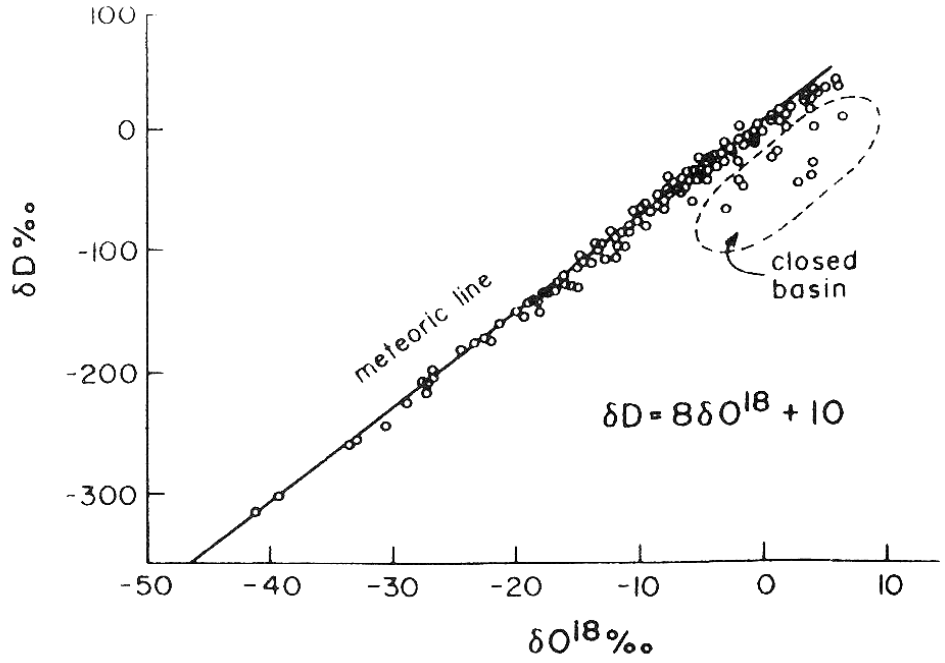

Figure 2. Global Meteoric Water Line. Isotopic compositions of ^{2}H and ^{18}O of water samples of rain, snow and other surface water bodies worldwide, yield a linear relationship between the isotopes characterized by the Global meteoric Water Line ($\delta^{2}H = 8\delta^{18}O + 10‰$). Compositions characterizing the closed basin are derived from water samples collected from Eastern African lakes, which are highly subject to evaporation [Craig, 1961; Mazor, 2004].

1.3.2 Local Meteoric Water Lines

The Global Meteoric Water Line is formed by the isotopic compositions of a combination of precipitation based water samples (rain, snow, rivers, lakes), which serves as a reference line for the determination of water sources and physical processes affecting isotopic compositions of meteoric waters (See Section 1.2). Depending on the region, differences in the amount of precipitation, temperature variations, distinct air mass sources, evaporation and fractionation processes occurring below the cloud base are characteristic at a local scale, which cause the relationship between stable isotopes of water δ^2H and $\delta^{18}O$ to vary from that of the Global Meteoric Water Line [Hoefs, 2004]. The particular isotope compositions for each region form Local Meteoric Water Lines (LMWL) that have different slopes and deuterium excess values than the GMWL, thus characterizing the compositions at the local scale [Clark and Fritz, 1997; Kendall and McDonnell, 1998; Aggarwal et al., 2005]. In this study the Rocky Mountain Meteoric Water Line ($\delta^2H = 8.1\delta^{18}O + 14.8‰$) is used as the local meteoric water line [A. Mast, personal communication, 2010] (Figure 3).

1.3.3 Slope of Experimental Lines

During evaporation, isotopic fractionation occurs under non-equilibrium conditions between the vapor-liquid phases, affecting the ratio of fractionation factors of the stable isotopes of water [Kendall and McDonnell, 1998]. When evaporation has occurred, fractionation factors are variable and isotope compositions become enriched in the heavier isotope forms relative to those of the GMWL or LMWL and thus forms

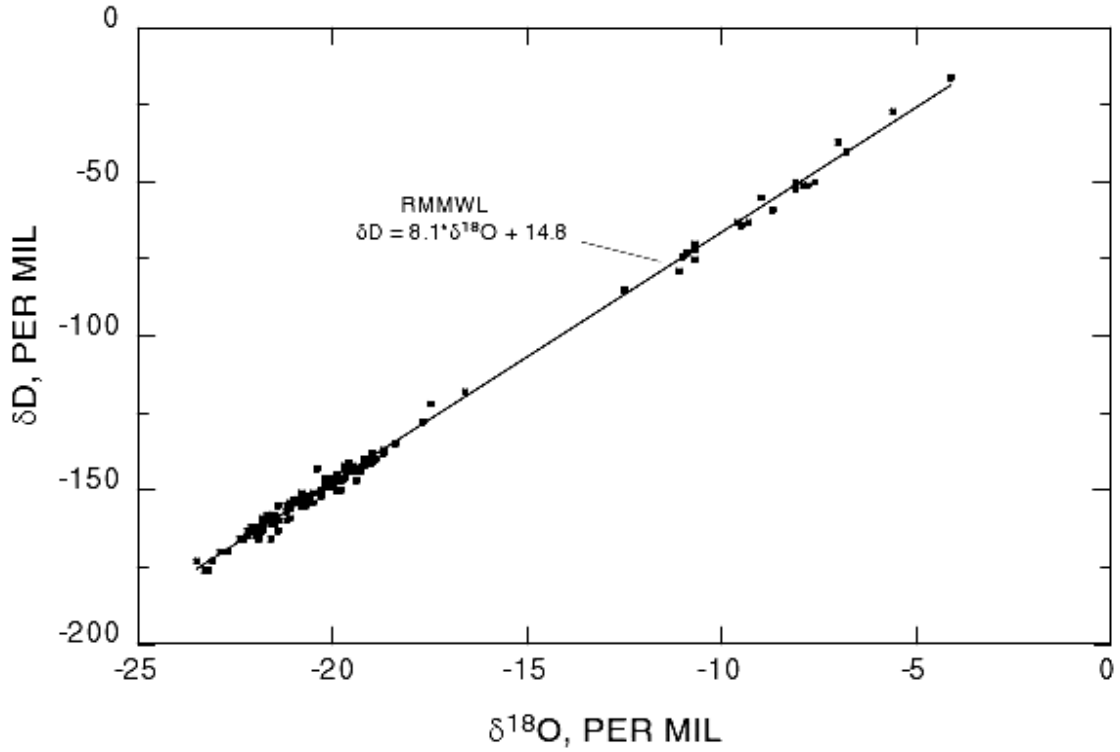

Figure 3. Rocky Mountain Meteoric Water Line. Local meteoric water line, RMMWL: $\delta^2H = 8.1\delta^{18}O + 14.8‰$, characterizing the isotopic compositions of water samples in the Rocky Mountain region, Colorado [A. Mast, personal communication, 2010].

experimental lines with different isotopic composition than those of the GMWL or the LMWL [Kendall and McDonnell, 1998]. Isotopic compositions that have been affected by evaporation usually plot below the GMWL and form experimental lines with a slope lower than that of the GMWL or LMWL, generally from 4 to 7 [Bowen, 1986; Kendall and McDonnell, 1998].

1.4 Previous Studies

In previous studies, the quantification of stable isotope compositions in river water and groundwater has been used as a method to determine evaporation rates and the contribution of sources of water to a semi-arid river system characterized by low precipitation, high temperatures, relatively gentle changes in elevation, high evaporation rates, agriculture as a common practice and diversions along the river are existent [Simpson and Herczeg, 1991; Datta et al., 1996; Horst et al., 2007; Kattan, 2007].

For example, in a study conducted in the Delhi area in India, stable isotope compositions and water chemistry of groundwater were examined to trace flow paths, mixing with other isotopically different waters, evaporation rates and the effect these have on chloride concentrations in a system where this source of water is the main supply for agriculture, drinking water and industrial practices [Datta et al., 1996]. Changes observed in ^{2}H and ^{18}O compositions through time and chloride concentrations in groundwater provided information to conclude river water and other sources of water (e.g., rainfall, surface runoff, irrigation return flows) with different isotope compositions compose and contribute to the mix of groundwater found in the area. Isotope compositions in groundwater are also determined by evapo-transpiration process and

temperature-dependent isotope exchange with rocks (^{18}O) that affect irrigation return flows and rainfall infiltrated through the unsaturated zone, which eventually mix and form part of deeper groundwater [Horst et al., 2007].

Like in groundwater, stable isotope compositions and chloride concentrations can also be used to determine the contribution sources of water with different isotope compositions have on a river system [Hem, 1992]. In the River Murray, Australia, stable isotope compositions of water and chloride concentrations were used to estimate evaporation rates and determine the contribution of irrigation return flows (water source) with temporal and spatial variations [Simpson and Herczeg, 1991]. Enrichment of ^{2}H and ^{18}O was observed both spatially and temporally, with the highest variation of the isotope compositions occurring in the summer, implying that the amount of enrichment was higher as a product of enriched tributary influx, high evaporation rates from surface water and influx of enriched irrigation return flows [Simpson and Herczeg, 1991].

Similar to the River Murray, the Euphrates River Basin is a semiarid – arid system characterized by cool and rainy winter seasons and warm and dry summer seasons, leading to the interest of utilizing stable isotope compositions of water to identify several sources of water and kinetic processes affecting the river [Kattan, 2007]. In the Euphrates River, stable isotope compositions and chloride concentrations were monitored to determine spatial or temporal variations that would indicate evaporation rates and irrigation return flow contributions [Kattan, 2007]. Isotopic enrichment as a result of evaporation and increasing chloride concentrations were seen with distance downstream suggesting the contribution of irrigation return flows and enriched tributary waters.

In the South Platte River, no previous studies of stable isotope compositions of the river water has been found. However, stable isotope compositions of precipitation in the Pawnee Grasslands of northeastern Colorado, located in the Great Plains Province have been examined [Harvey, 2005]. Stable isotope compositions of precipitation in this area showed a positive correlation between δ^2H and $\delta^{18}O$ compositions thus forming a local meteoric line $\delta^2H = 7.86\ \delta^{18}O + 7.66$ ‰) with heavier isotope values than those of the global meteoric water line. Compositions in precipitation during the winter season showed to be depleted relative to those of the summer season resulting from changes in temperature, different vapor sources, different site elevations and changes in evaporation that vary seasonally.

1.5 Problem Statement

The South Platte River (SPR) is a semi-arid hydrologic system running from central to northeastern Colorado, that supplies water to maintain and promote economical and population development as large volumes of water are extracted from the river for the use of municipalities, industries and agricultural lands. Throughout history, the South Platte River was known as an ephemeral system with dry periods during the summer and high river flow during the spring; however, with the development of reservoirs and diversions, flow has been regulated and controlled transforming the river into a perennial system [Camp Dresser and McKee, 1994]. Discharge along the South Platte River is composed of several sources of natural and anthropogenic origin that contribute different volumes to streamflow and affect water quality of the river water through time and space. These contributing sources include rainfall, urban and agricultural runoff, snowmelt,

wastewater effluent, irrigation return flows, tributaries and reservoirs. Flow levels in the SPR vary during different seasonal periods as these various water sources discharge into the system in diverse quantities as a function of time and space. Stable isotopes compositions will be used to identify the effect evaporation and water sources have in the river water through space and time.

1.6 Hypotheses

In order to determine the effect evaporation and water sources have in the river water, stable isotope compositions will be examined through space and time in the South Platte River. Four hypotheses will be tested: 1) Stable isotope $\delta^{2}H$ and $\delta^{18}O$ compositions of the South Platte River water will become enriched with increasing distance downstream due to evaporation; 2) If sources of water to the river have different isotope compositions than those of the South Platte, then the isotope compositions along the river will be affected by the contribution of these; 3) If sources of water to the South Platte change over time, then the isotope compositions of the river will be affected by the change in isotope compositions of the water sources; 4) Isotope compositions of the South Platte River will vary during different flow periods due to a change in water sources.

1.7 Objectives

Three main objectives will be examined: 1) Determine if stable isotope compositions change spatially along the river. 2) Determine if stable isotope compositions change temporally along the river. 3) Determine if stable isotope compositions of water vary between low and high flow periods of the South Platte River.

Chapter 2

SITE DESCRIPTION

The South Platte River, in northeastern Colorado, supplies river and alluvial water for agricultural, industrial and potable demands. With a total drainage area of ~ 62,900 km^2 (24,300 mi^2), approximately 80% of the South Platte River basin lies in Colorado [Litke and Kimbrough, 1998]. Originating in the Central Colorado Rocky Mountains, the river flows to the northeast through the state towards southwest Nebraska, where it meets the North Platte River, forming the Platte River [Litke and Kimbrough, 1998] (Figure 4). Depending on elevation, precipitation in the basin is variable with approximately 76.2 cm/year (30 in/year) received in the mountainous areas as rain and snow and 38.1 cm/year (15 in/year) received in the plains area as rainfall, mainly in the form of thunderstorms, from April to September [Dennehy et al., 1998] (Figure 5). The river flow in the South Platte is seasonally dependent with high river flow caused by snowmelt contribution during the spring and a low river flow during the summer [Harris, 1993].

The land use of the basin is categorized to be ~41% rangeland, 37% agricultural land, 16% forestland and 3% urban land [Litke and Kimbrough, 1998] (Figure 6). Besides snowmelt from the Central Colorado Rocky Mountains, water diversions from

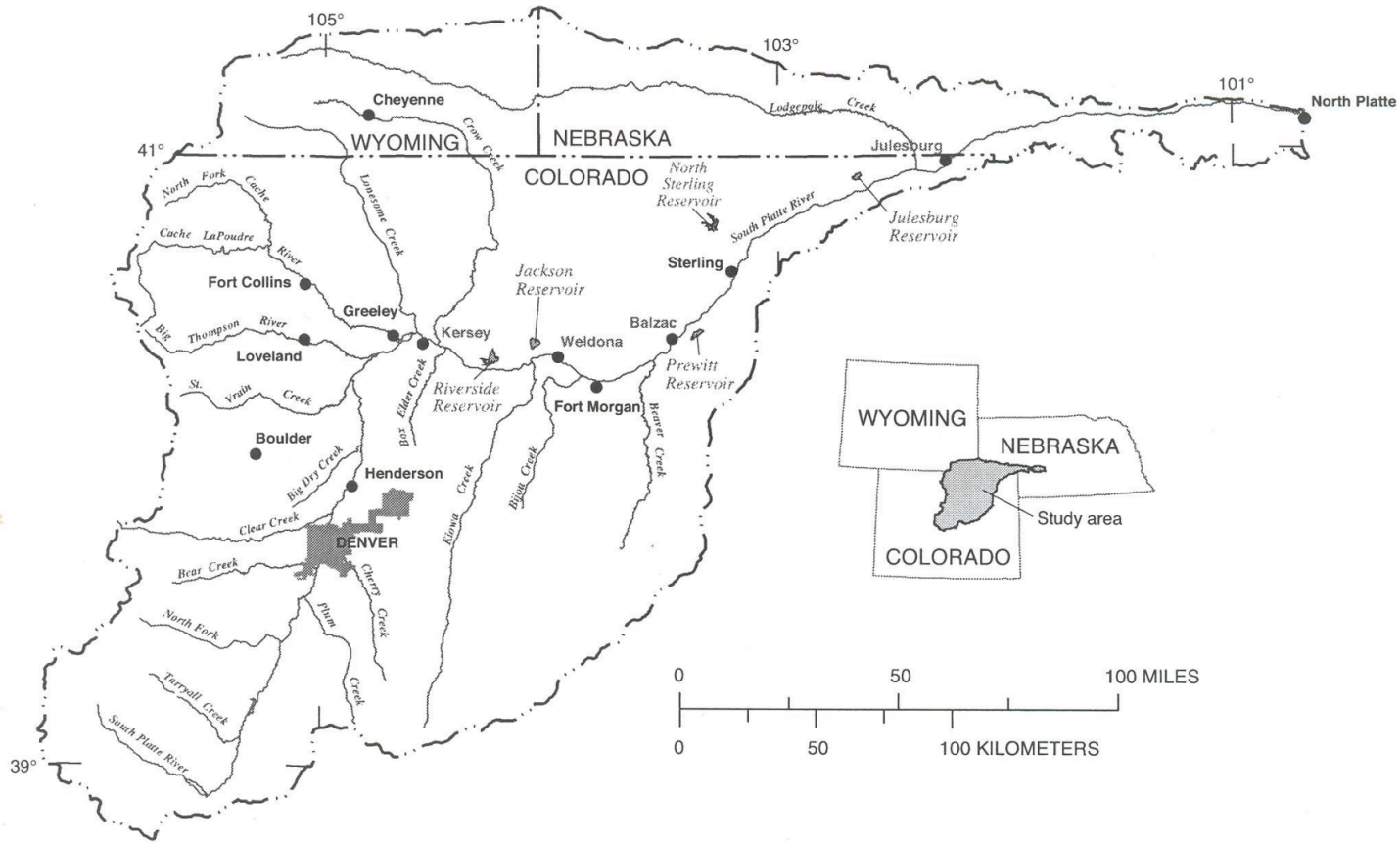

Figure 4. South Platte River Basin and its Main Tributaries [Sprague et al., 2002].

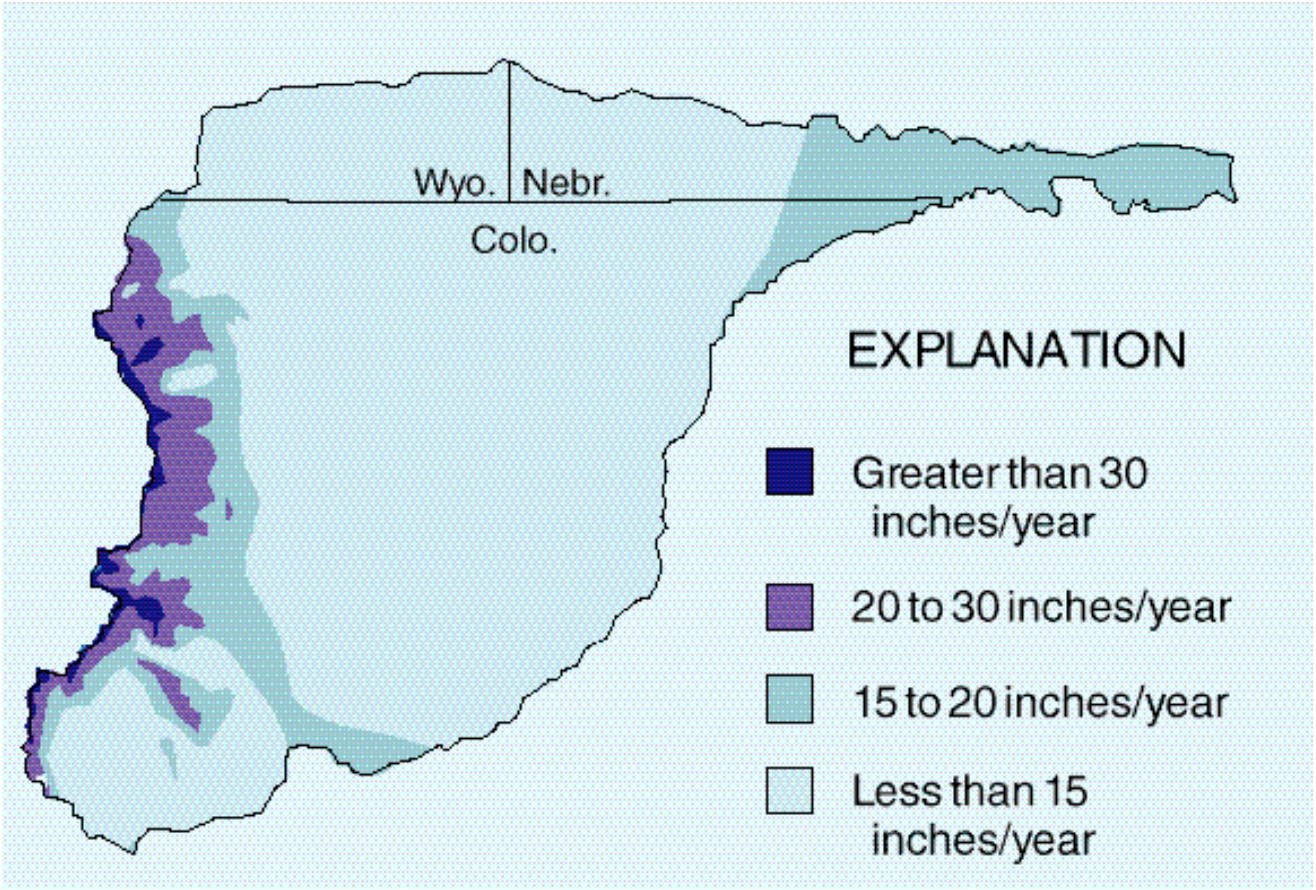

Figure 5. Precipitation in the South Platte River Basin [South Platte River Hydrologic Observatory: http://www.engr.colostate.edu/~ramirez/SouthPlatte_LTHO.htm].

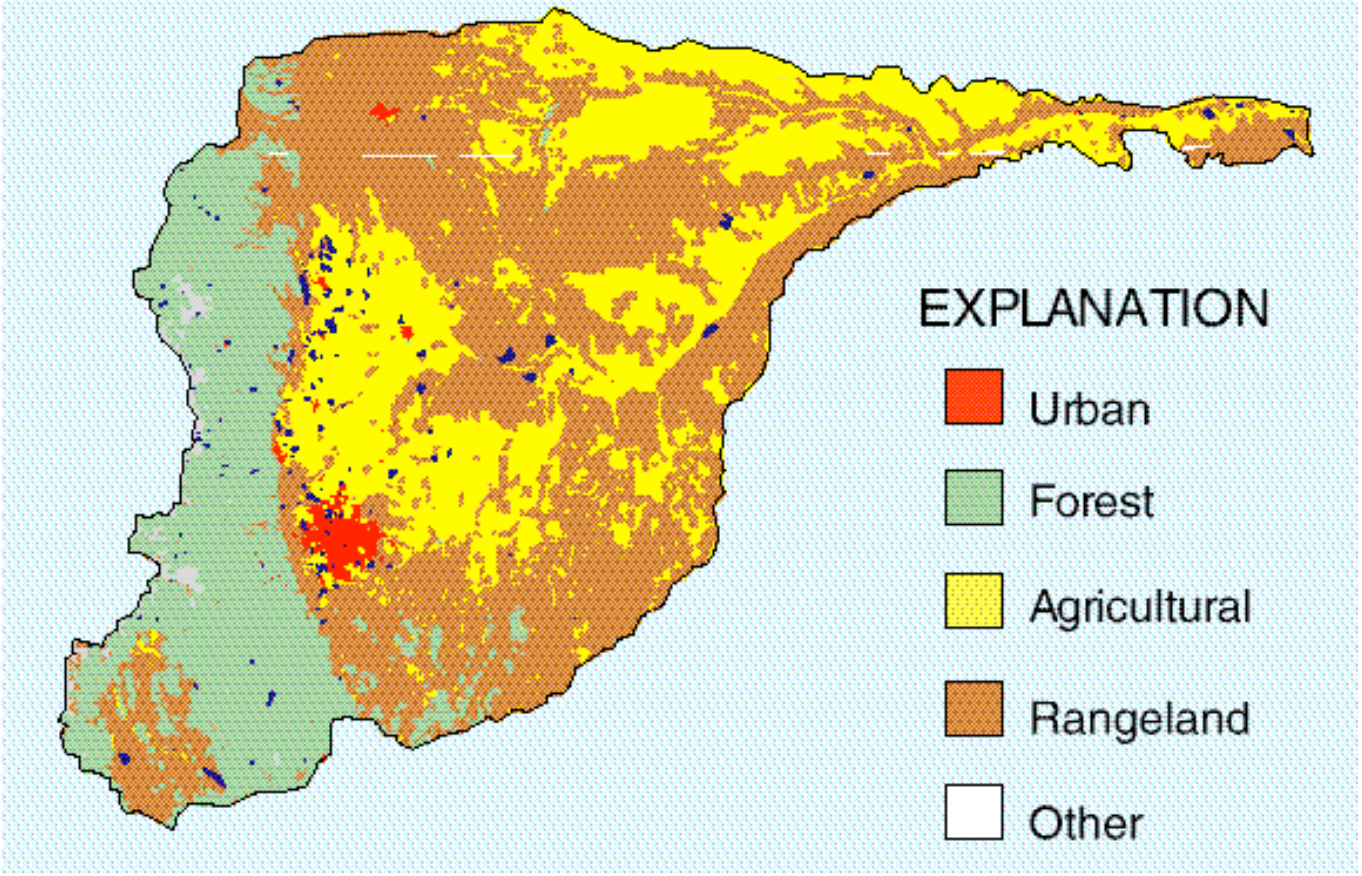

Figure 6. Land use in the South Platte River Basin [South Platte River Hydrologic Observatory: http://www.engr.colostate.edu/~ramirez/SouthPlatte_LTHO.htm].

west of the Continental Divide import water from the Colorado, Arkansas and North Platte River Basins into the South Platte River Basin [Sprague, 2005]. It is estimated that within the basin, on an annual basis, 3.7 km^3 (3 million acre-feet) of water is diverted to irrigation structures, 2.5 km^3 (2 million acre-feet) of water is accumulated in reservoirs, ~ 0.5 km^3 (400,000 acre- feet) of water are transported from 12 transmountain diversions and ~1.2 km^3 (1 million acre- feet) of water are pumped from the alluvial aquifer [Dennehy et al., 1998].

2.1 Geologic Setting

The South Platte River basin lies within two physiographic provinces: The Southern Rockies Province which comprises 25% of the total basin surface area (western) and the remaining 75% of the basin (eastern) is within the Great Plains Province [Litke and Kimbrough, 1998]. There are two primary rock types that form the basin: Precambrian crystalline rock that underlies most of the Southern Rockies Province and a younger sedimentary rock that underlies most of the Great Plains Province [Litke and Kimbrough, 1998]. Sedimentary rock underlying the valleys and plains formed by the Rocky Mountains are shale, limestone and sandstone beds formed during the Cretaceous and Tertiary periods [Webb and Rockwell, 1974].

In the plains area, the valley fill is composed of silt, clay, gravel and sand of the Pleistocene and Holocene epochs, with thicknesses ranging from 15 to 61 meters (50 to 200 feet) [Webb and Rockwell, 1974]. Sedimentary rock deposited during the Paleozoic, Mesozoic and Cenozoic Eras, with cumulative thickness of more than 5,486 meters (18,000 feet), extend from the foothills of the Rocky Mountains to the outermost eastern

(18,000 feet), extend from the foothills of the Rocky Mountains to the outermost eastern extension of the basin [Webb and Rockwell, 1974]. The Great Plains Province comprising eastern Colorado is composed of gravel terraces, alluvium, sand dunes and loess sediments deposited during the Wisconsin Glacial Period that have been shaped throughout thousands of years by the course of the braided river [Webb and Rockwell, 1974]. The reach of the river from Henderson to Julesburg is situated in the Great Plains Province. Underlying the South Platte River at Henderson CO, is Lower Tertiary to Upper Cretaceous sandstone and shale of the Denver Formation; in Kersey CO, the sediments are mainly Upper Cretaceous sandstone with alluvial deposits up to 46 meters (150 feet) and in Balzac, CO (~ 119 kilometers downstream of Kersey), the sediments are Upper Cretaceous sedimentary rocks, mainly sandstone and dark organic-rich Pierre Shale that underlies the river alluvium close to Fort Morgan [Litke and Kimbrough, 1998].

2.2 Alluvial Aquifer

The gravel, sand and alluvial sediments deposited through the years in the South Platte River Basin have formed an alluvial aquifer with a total area of 10,360 km^2 (~2.5 million acres) that is hydraulically connected to the river [Litke and Kimbrough, 1998]. Coarse-grained sediments (gravel) mainly compose the alluvial aquifer in the western part of the basin (mountainous area), while sediments towards the eastern part of the basin (plains area) become finer grained (sand), forming thicker alluvial deposits in this part of the basin [Bruce and McMahon, 1998]. Water table depths in the alluvial aquifer range from 0 to 12 meters (0 to 39 feet) and hydraulic conductivity values range from 30

to 600 meters/day (100 to 2000 feet/day) [Kimbrough and Litke, 1998]. At Henderson, alluvial deposits reach a thickness of up to 12 meters (39 feet), 45 meters (150 feet) at Kersey, 61 meters (220 feet) at Weldona, from 15 to 85 meters (50 to 280 feet) at Fort Morgan, 67 meters (220 feet) at Sterling and 91 meters (300 feet) from Sterling to Julesburg [Webb and Rockwell, 1974; Litke and Kimbrough, 1998].

2.3 Agricultural Uses

Agriculture is the primary use of lands within the Great Plains Province in northeastern Colorado (Figure 6). Even though only 8% of the basin surface area consists of irrigated agricultural land and 3% of urban land, 71% of water use is for irrigation and 12% for urban land usage [Dennehy et al., 1998]. Of the total ~62,900 km^2 (15 million- acres) land area of the South Platte River basin, ~23,000 km^2 (5.7 million-acres) is crop and pastureland (agricultural land); of which ~12,000 km^2 (3.0 million-acres) is non-irrigated pastureland, ~6,500 km^2 (1.6 million-acres) is dry-land farming and ~4,400 km^2 (1.1 million-acres) is irrigated crop and pastureland [Bruce and McMahon, 1998]. A total of 3.8 km^3 (3.1 million acre-feet) of water is used annually for irrigation in the South Platte River basin, of which ~1.6 km^3 (1.3 million acre-feet) discharge into the stream as irrigation return flows and 1,100 km^2 (250,000 acres) are irrigated with groundwater [Dennehy et al., 1993].

into the SPR, creating a challenge for humans to not violate water quality standards required for clean and potable water [Gaydos, 1981]. More than 160 municipal waste discharge point sources of mainly domestic waste discharge their effluent into the South Platte River, a tributary of the river or through the land as groundwater via percolation ponds, leach fields and septic tanks [Webb and Rockwell, 1974]. Of these point sources, 76 treatment plants discharge significant volumes of water to the river of which 13 have been classified as major dischargers (effluent is higher than 0.8 ft^3/s (cfs)), several of which are located at Fort Morgan, Greeley and Sterling, CO [Webb and Rockwell, 1974].

Several of the minor dischargers (effluent is less than 0.8 ft^3/s) are located in Platteville, Evans, Kersey, Merino, Crook, Ovid and Julesburg [Webb and Rockwell, 1974]. Of the totality of wastewater treatment plants in the basin, 25 are located along the Front Range, with the largest treatment plant located at Denver, CO [Dennehy et al., 1998]. Approximately 428 ft^3/s (275 million gallons/day) of wastewater effluent are discharged into the basin by these 25 treatment plants, which constitutes ~ 95% of the effluent discharged daily [Pocernich and Litke, 1997; Dennehy et al., 1998]. The Central Treatment Plant effluent from the Denver metro-area comprises from ~69 to 90 % of the river flow for almost 9 months of the year from Denver to near Fort Lupton, CO [Camp Dresser and McKee, 1994; Dennehy et al., 1998; http://www.metrowastewater.com]. Even though the Metro Wastewater Reclamation District discharge into the river constitutes a 90% of the flow during much of the year, the effect produced by this effluent is not distinguishable 48 kilometers (30 miles) downstream of Denver [Harris, 1993].

constitutes a 90% of the flow during much of the year, the effect produced by this effluent is not distinguishable 48 kilometers (30 miles) downstream of Denver [Harris, 1993].

Chapter 3

METHODS

Water samples were collected along the South Platte River, from Henderson to Julesburg, the Big Thompson and Cache la Poudre Rivers and Riverside and Jackson Lake Reservoirs to characterize stable isotope compositions of the river water under various environmental settings (Figure 7). Sampling locations were chosen to be indicative of the different environmental settings (urban; urban and agricultural/rangeland; and agricultural/rangeland) present in the basin [Litke and Kimbrough, 1998] (Figure 6). From Henderson to Julesburg, CO, the course of the river crosses three main environmental settings (Table 1), though most of the sampling locations in this study are located in an agricultural/ rangeland setting (Evans to Julesburg).

Agriculture is the predominant use of land in northeastern Colorado, which generate the necessity of diversions and storage reservoirs to meet water demands while maintaining river flow through time [Camp Dresser and McKee, 1994]. To understand the availability and quality of the water transported through these agricultural lands and that can be utilized for irrigation, the role of contributing tributary influx and storage

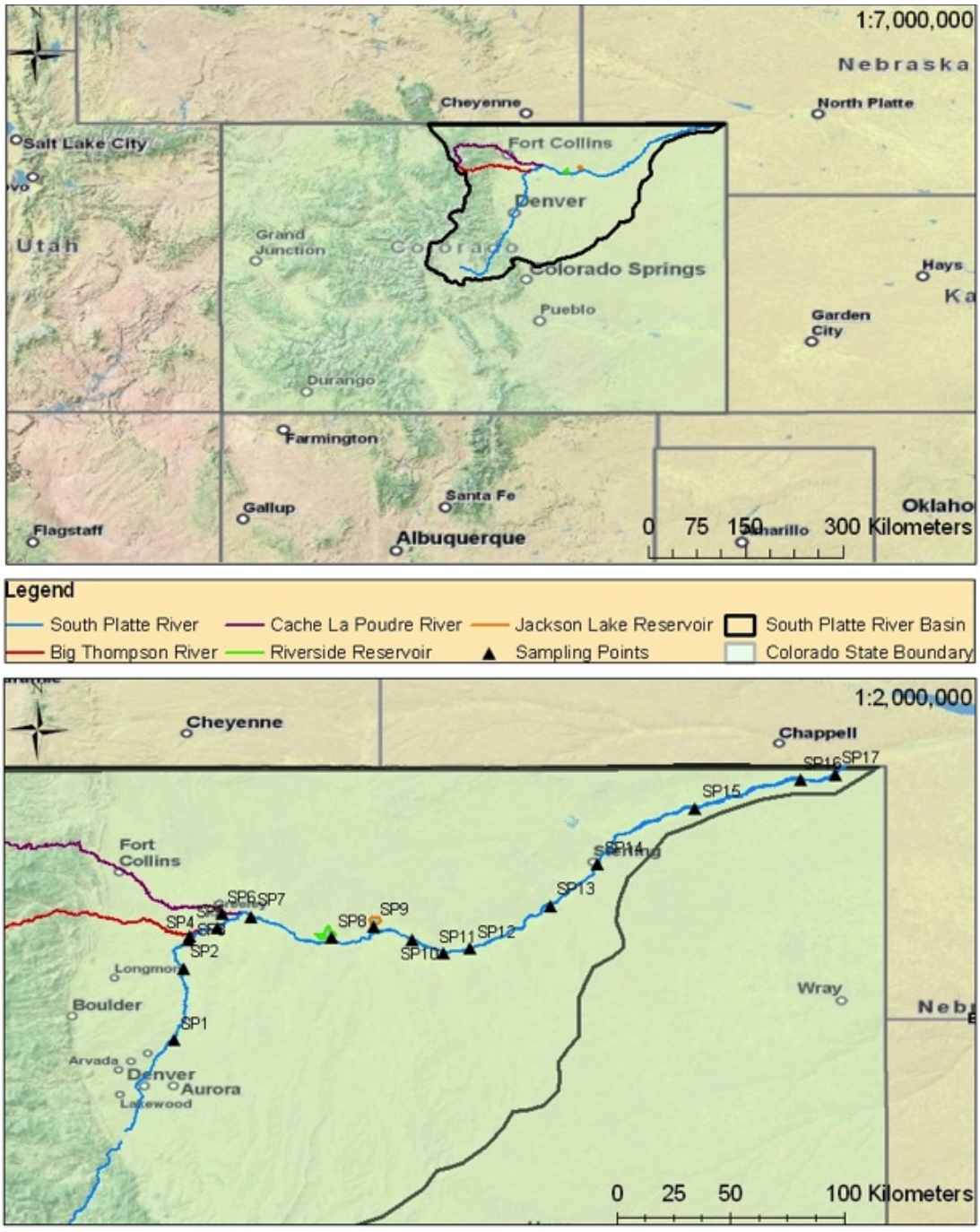

Figure 7. Sampling Locations. 13 sample locations along the South Platte River, one at the Big Thompson River, one at Cache la Poudre River, one at Riverside Reservoir and one at and Jackson Lake Reservoir.

Table 1. Sampling Locations and their Environmental Setting. List of the 17 sample sites located along the South Platte River, with the initial sampling point at Henderson (0 km) and the final location at Julesburg (291 km). Distance downstream from Henderson and the predominant environmental setting are listed for each location.

Original Code	Location	Distance Downstream (kilometers)	Environmental Setting
SP1	Henderson	0	Urban
SP2	Platteville	32	Urban/Agricultural
SP3	Big Thompson River	47	Agricultural
SP4	Rd 60, Above confluence	44	Agricultural
SP5	Evans, Below confluence	55	Agricultural
SP6	Poudre River, Greeley	58	Agricultural
SP7	Downstream Poudre River, Kersey	68	Agricultural
SP8	Riverside Reservoir, Masters	70	
SP9	Jackson Reservoir	84	
SP10	Weldona	123	Agricultural
SP11	Ft. Morgan	135	Agricultural
SP12	Dodd Bridge Rd, Wildlife	144	Agricultural
SP13	Bridge west of Merino	177	Agricultural
SP14	Sterling	201	Agricultural
SP15	Crook	242	Agricultural
SP16	Ovid	279	Agricultural
SP17	Downstream Julesburg	291	Agricultural

reservoirs to the South Platte River flow needs to be considered [Gaydos, 1981]. In the study area, the tributaries the Big Thompson River and the Cache la Poudre River provide water that has been transported through a mountain/forestland area that discharges to the South Platte close to the cities of Evans and Greeley (Figure 7). The Big Thompson River originates in the Rocky Mountains and even though it crosses mainly a forestland setting, the river mouth (close to Evans) is characterized by an agricultural/rangeland setting; the Cache la Poudre River, originating in the Rocky Mountains, crosses a forestland setting as well, but is also transported through the urban land setting of the city of Fort Collins and the agricultural/rangeland setting of Greeley, where it discharges to the main channel [Litke and Kimbrough, 1998] (Figure 4). Also affecting water quality is the presence of reservoirs such as Riverside Reservoir and Jackson Lake Reservoir, which discharge into the South Platte River (Figure 4).

3.1 Sample Locations

Water samples were collected at 17 different locations, of which 13 sites were located along the South Platte River, from Henderson to Julesburg, CO, one near the mouth of the Big Thompson River, one near the mouth of the Cache la Poudre River, one at Riverside Reservoir and one at Jackson Lake Reservoir (Figure 7). The initial sampling site at Henderson, CO, is characterized by an urban setting, located approximately 31 kilometers (19 miles) downstream of the Denver metropolitan area (Figure 7). Due to the proximity of the Denver metropolitan area and Henderson, Colorado, the usage and management of the river water in the urban setting, such as wastewater treatment plant effluent, tributary influx, channelization of the river,

industrial waste, runoff, dams and storage reservoirs should affect river water downstream at Henderson. The Metro Wastewater Reclamation District, which regulates all wastewater treatment for the Denver-metro area is located ~ 21 kilometers (13 miles) upstream of Henderson, CO (Figure 7). Downstream of the initial sampling site, locations were selected for the transition between environmental settings (e.g., urban: Henderson; urban and agricultural/rangeland: Platteville; agricultural/rangeland: Sterling) and the effect of tributary and reservoir water influx (e.g., downstream Big Thompson River: Evans; downstream Cache la Poudre River: Kersey; downstream Riverside and Jackson Lake Reservoirs: Weldona) (Table 1).

Sampling sites at the Big Thompson River and the Cache la Poudre River were selected to represent tributary influx to the South Platte River. Riverside Reservoir is located approximately 35 kilometers (22 miles) downstream of Kersey, CO and Jackson Lake at approximately 13 kilometers (8 miles) upstream of Weldona; both reservoirs are located in an agricultural/rangeland setting and serve the purpose of storing water to supply and control this resource during the irrigation season and for flow augmentation (Figure 7). The final sampling site at Julesburg, ~3 kilometers (2 miles) from the state line with Nebraska, characterizes an agricultural/rangeland setting. At Julesburg, river water is characterized by the collective effect of diverse processes that occurred upstream such as the transition between the different environmental settings, the mixing of tributary influx and water released from storage reservoirs, irrigation ditches, diversions, irrigation return flows and snowmelt with already present river water in the South Platte.

3.2 Sampling over the Annual Hydrograph

In order to measure the effect of the irrigation and non-irrigation seasons on water quality, it was necessary to select dates that would represent the variability of flow levels and water usage through these seasons. In the South Platte River Basin, the irrigation season occurs from March to September and from October to March, storage reservoirs start to fill (Sprague et al., 2002). In the basin, discharge is high during the spring and early summer (April to June) as high volumes of snowmelt from the Central Rocky Mountains are discharged. From July to March discharge in the river is low. During July through September (irrigation season), low discharge is caused by the diminishing contribution of snowmelt received from the Central Rocky Mountains; while during the non-irrigation season (October to March) wastewater effluent mainly contributes discharge and maintains a low flow in the river.

Nine sampling dates were chosen to represent high and low flow during the irrigation season and the low flow during the non-irrigation season. The first sampling date was in June 2009, with a peak discharge followed by a sampling date in July 2009, on the falling limb of the hydrograph. A sampling date was chosen in September 2009 to represent the end of the irrigation season. Samples were collected in October 2009, January and February 2010 to indicate low flow during the non-irrigation season. Sample dates in April, May and June 2010 were selected to characterize variations during the transition between the non-irrigation and irrigation seasons and also between high flow and low flows within the irrigation season. During these months, snowmelt caused a rising limb in the hydrograph, reaching a peak in June 2010.

3.3 Sample Collection

At every site, water samples were collected in two high-density polyethylene (HDPE) bottles that were triple rinsed with river water prior to sample collection. Samples for stable isotope analysis were collected in 20 mL scintillation vials while samples for water quality analysis were collected in 250 mL Nalgene® bottles. For each sample, the bottle was entirely submerged underwater and the cap tightly sealed in order to minimize any air in the bottle. Several physical parameters were measured at each site: pH, temperature (°C) and specific conductance (μS). Specific conductance and temperature readings were obtained by utilizing a Eutech® specific conductance probe, pH was measured with a Hanna® pH meter and location and altitude by utilizing a Garmin® GPS. Samples were collected from the edge of the river in moving water where mixing most likely had occurred. After the collection of the sample, the bottles were stored in a cooler with ice packs; upon returning from the field, samples were refrigerated.

3.3.1 Duplicate Samples

Within every sampling round, two duplicate samples were collected at two random locations out of the 17 sampling locations. The Relative Standard Deviation (%RSD) was measured for every duplicate sample.

RDS = (standard deviation of array x / average of array x) x 100 (2),

where array x= (original sample: duplicate sample). This calculation allows for the direct comparison of the duplicate sample isotope compositions to the original sample isotope compositions on a certain location along the river. For example:

RDS = (standard deviation (δ^2H A6: δ^2H A7) / average (δ^2H A6: δ^2H A7)) x 100

and

RDS = (standard deviation (δ^{18}O A6: δ^{18}O A7) / average (δ^{18}O A6: δ^{18}O A7)) x 100

3.4 Laboratory Procedure

Following the sample collection in the field, water samples were analyzed for stable isotope compositions (δ^2H and δ^{18}O). Stable isotopes compositions are reported with respect to VSMOW in parts per mil (‰) as mentioned in Section 1.1.1. Stable isotope compositions were determined at the University of Wyoming Stable Isotope Facility (SIF).

3.4.1 Stable Isotopes of δ^2H and δ^{18}O

All 20 mL disposable scintillation vials were tightly sealed around the cap with Parafilm Laboratory Film, labeled with its corresponding sampling site identification number (Table 2), packed within a week after collection and sent to the Stable Isotope Facility (SIF) at the University of Wyoming. Stable isotope (δ^2H and δ^{18}O) compositions were analyzed at SIF by using Los Gatos laser liquid water analyzer [http://uwacadweb.uwyo.edu/sif/].

Table 2. Sampling Locations Identification Key. List of the 17 sampling locations and their identification codes. Each location is labeled with a unique code starting with SP (standing for South Platte) and later were relabeled for a unique code within each round from the first round (A samples) to the last round (I samples). During each round, two duplicates were collected at random locations, which are also included.

	Sampling Date	6/19/09	7/17/09	9/17/09	10/22/09	1/21/10	2/23/10	4/15/10	5/20/10	6/18/10	
Original Code	**Location**	**Round 1**	**Round 2**	**Round 3**	**Round 4**	**Round 5**	**Round 6**	**Round 7**	**Round 8**	**Round 9**	**Duplicates**
SP1	Henderson	A1	B1	C1	D1	E1	F1	G1	H1	I1	F2
SP2	Platteville	A2	B2	C2	D2	E2	F3	G2	H2	I2	E3
SP3	Big Thompson River	A3	B3	C3	D3	E4	F4	G3	H3	I3	G4
SP4	Rd 60, Above confluence	A4	B4	C4	D4	E5	F5	G5	H4	I4	D5
SP5	Evans, Below confluence	A5	B5	C5	D6	E6	F6	G6	H5	I5	B6
SP6	Cache la Poudre River, Greeley	A6	B7	C6	D7	E7	F7	G7	H6	I6	A7, I7
SP7	Kersey, CO	A8	B8	C7	D8	E8	F8	G8	H7	I8	F9, H8
SP8	Riverside Reservoir	A9	B9	C8	D9	E9	F10	G9	H9	I9	
SP9	Jackson Reservoir	A10	B10	C9	D10	E10	F11	G10	H10	I10	
SP10	Weldona	A11	B11	C10	D11	E11	F12	G11	H11	I11	E12
SP11	Ft. Morgan	A12	B12	C11	D12	E13	F13	G12	H12	I12	C12
SP12	Dodd Bridge Rd, Wildlife	A13	B13	C13	D13	E14	F14	G13	H13	I13	G14
SP13	Bridge west of Merino	A14	B14	C14	D14	E15	F15	G15	H14	I14	H15
SP14	Sterling	A15	B15	C15	D15	E16	F16	G16	H16	I15	B16
SP15	Crook	A16	B17	C16	D16	E17	F17	G17	H17	I16	D17
SP16	Ovid	A17	B18	C17	D18	E18	F18	G18	H18	I17	A18, I18
SP17	Julesburg	A19	B19	C18	D19	E19	F19	G19	H19	I19	C19

Chapter 4

RESULTS

Water samples were collected from Henderson to Julesburg at the South Platte River, from June 2009 to June 2010, a period in which discharge in the river varied both spatially and temporally (Table 3). At Henderson (SP1), the lowest mean discharge of ~750 ft^3/s was observed with a general increase downstream towards generally increase towards Kersey (SP7), where the highest mean discharge of ~2100 ft^3/s was observed (Table 3). Discharge along the South Platte River, Big Thompson River and Cache la Poudre River also varied as a response to seasonal periods, when the highest volumes occurred in June of 2010 and the lowest volumes in July of 2009 (Table 3). In this study, the annual hydrograph at Fort Morgan, CO is referenced to describe discharge changes along the South Platte River during the different sampling events (Figure 8). Flow levels at Fort Morgan ranged from as low as 120 to the highest flow of 8650 ft^3/s. Peak flows of 2800 and 8650 ft^3/s were observed in June 2009 and June 2010 while low flows ranged from 120 to 340 ft^3/s from July 2009 to April 2010 (Table 3).

Table 3. List of daily discharge volumes (ft^3/s) at Henderson, Kersey, Weldona, Fort Morgan, Crook and Julesburg. Also included are daily discharge volumes of the Big Thompson River (BTR) near the mouth at La Salle, CO and the Cache la Poudre River (CLPR) near Greeley, CO [www.lspwcd.org].

Sample Month	Henderson	BTR	CLPR	Kersey	Weldona	Fort Morgan	Crook	Julesburg
6/19/09	1520	38	756	3710	3030	2770	3590	2180
7/17/09	452	22	61	251	160	187	67.1	381
9/17/09	265	35	103	526	206	232	251	299
10/22/09	606	56	85	929	247	289	475	510
1/21/10	48.7	69	165	549	260	338	1780	668
2/23/10	272	75	105	507	108	138	167	268
4/15/10	355	30	124	653	141	123	304	394
5/20/10	1260	494	1050	4450	3330	3150	3140	2220
6/18/10	1980	662	2140	7430	8290	8650	6820	4080
Average	751	165	510	2112	1752	1764	1844	1222

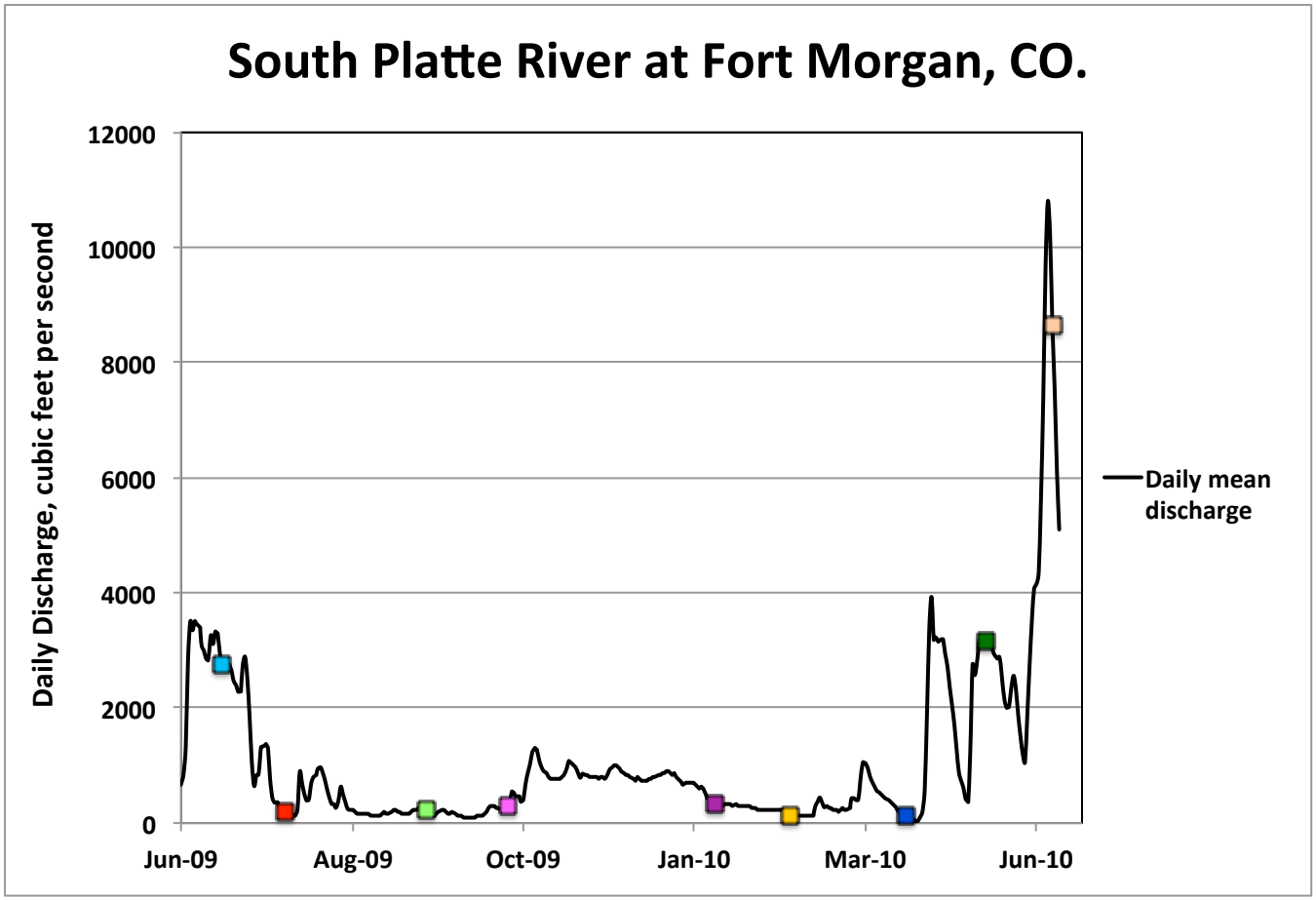

Figure 8. Discharge of the South Platte River at Fort Morgan, CO during June 2009 to June 2010. Nine sampling rounds (rectangles) were collected during different discharge levels at Fort Morgan through the one-year period [Source: *USGS Surface-Water Daily Data for Colorado;* http://waterdata.usgs.gov/co/nwis/dv?].

4.1 Stable Isotope Compositions

During the one-year sampling period, a total of 171 water samples were collected and analyzed for stable isotopes compositions of water (Table 4). Out of these water samples, 18 samples were duplicate samples that showed isotope compositions similar to those of the original samples determined by low values of relative standard deviations (RSD %) ranging from 0 to 1.2 % δ^2H and 0.1 to 4.8 % $\delta^{18}O$ (Table 5). Overall, throughout all sampling rounds, mean isotope compositions along the South Platte River from Henderson to Julesburg ranged from -110.2 ‰ to -94.5 ‰ δ^2H and from -14.4 ‰ to -12.0 ‰ $\delta^{18}O$ (Table 6 and Figure 9). On May 2010, two wastewater effluent samples were collected from the Metro Wastewater Reclamation District (MWRD) and yielded isotope compositions of -110.5 ‰, -107.9 ‰ δ^2H and -14.6 ‰, -14.2 ‰ $\delta^{18}O$ (Figure 10 and 11).

Within each sampling period, isotope compositions of the water samples along the South Platte River illustrated a strong positive correlation between δ^2H and $\delta^{18}O$ compositions with a general enrichment in heavy isotope compositions with distance downstream (Figures 9, 10 and 11). For all sampling rounds during 2009 - 2010, compositions plotted below the Rocky Mountain Meteoric Water Line, except two sampling points in June 2010. Even though most of the stable isotope compositions of the water samples plotted below the meteoric water lines, a distinct separation occurred in isotope compositions of water samples comprising the high flow period (June 2009, May and June 2010) relative to the compositions during the low flow period (Figures 10 and 11).

Table 4. Isotopic compositions (δ^2H and $\delta^{18}O$), within each sampling round for all seventeen sampling sites along the South Platte River, its tributaries and reservoirs. Isotopic compositions are reported in ‰ (per mil).

Sample	6/19/09		7/17/09		9/17/09		10/22/09		1/21/10		2/23/10		4/15/10		5/20/10		6/18/10	
	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
SP1	-115.0	-15.3	-105.1	-14.0	-104.3	-13.3	-119.1	-16.0	-107.4	-14.1	-110.2	-13.9	-106.5	-13.7	-108.4	-14.3	-115.7	-14.6
SP2	-113.9	-14.6	-104.2	-13.8	-102.4	-13.2	-109.9	-14.1	-104.6	-13.4	-107.0	-13.6	-106.6	-13.2	-106.4	-14.3	-114.5	-14.4
SP3	-108.0	-13.6	-106.1	-13.9	-105.2	-13.3	-105.0	-13.2	-112.3	-13.7	-112.9	-14.6	-105.4	-12.7	-113.2	-15.4	-121.9	-15.9
SP4	-116.5	-15.1	-104.9	-14.1	-104.0	-13.0	-107.4	-13.7	-110.6	-13.5	-106.9	-13.9	-107.4	-13.8	-110.8	-14.4	-116.6	-14.9
SP5	-116.5	-15.0	-103.7	-13.9	-103.5	-13.0	-106.1	-13.0	-110.4	-13.5	-107.7	-14.3	-105.7	-13.5	-110.4	-14.8	-117.3	-14.8
SP6	-124.2	-16.0	-101.8	-13.4	-102.5	-12.6	-101.0	-12.2	-109.5	-13.0	-105.3	-13.9	-105.5	-13.8	-115.0	-15.8	-125.9	-15.8
SP7	-118.2	-14.7	-103.1	-13.7	-103.2	-13.2	-104.8	-12.7	-109.6	-13.2	-106.4	-14.4	-106.8	-13.7	-111.9	-15.3	-120.9	-15.1
SP8	-99.5	-11.5	-97.5	-12.7	-88.5	-10.5	-96.2	-11.2	-99.5	-11.5	-99.2	-12.9	-103.3	-13.5	-98.6	-13.5	-100.4	-11.7
SP9	-84.4	-8.8	-80.8	-9.7	-71.1	-7.6	-69.4	-6.5	-84.2	-9.0	-82.8	-9.8	-82.8	-10.3	-80.1	-9.9	-78.1	-8.2
SP10	-113.5	-13.8	-99.0	-12.7	-97.0	-12.7	-97.9	-11.8	-101.3	-11.9	-97.8	-12.4	-98.7	-13.2	-108.0	-14.9	-118.1	-16.7
SP11	-113.3	-14.2	-60.4	-8.0	-96.3	-12.6	-97.5	-11.7	-101.5	-12.0	-97.9	-12.2	-99.4	-13.2	-107.3	-14.7	-116.7	-17.1
SP12	-112.0	-14.0	-95.0	-12.6	-96.3	-12.4	-97.8	-12.0	-100.7	-12.0	-97.4	-12.4	-98.5	-13.1	-106.4	-14.9	-117.0	-15.3
SP13	-110.2	-13.7	-90.7	-11.6	-93.7	-11.9	-97.2	-11.8	-96.2	-11.0	-95.8	-12.1	-96.1	-12.6	-105.6	-14.2	-103.1	-13.7
SP14	-109.3	-13.5	-96.0	-12.7	-96.4	-12.3	-96.3	-12.1	-93.1	-11.3	-96.7	-12.2	-93.6	-12.4	-104.9	-14.3	-114.0	-15.8
SP15	-106.8	-13.0	-94.6	-12.7	-89.3	-11.4	-95.0	-12.1	-96.2	-11.2	-93.4	-11.4	-92.6	-12.5	-101.1	-13.2	-111.8	-15.7
SP16	-103.6	-13.0	-91.4	-12.1	-87.7	-11.4	-92.6	-11.4	-95.4	-11.0	-89.9	-11.3	-92.1	-12.1	-99.2	-13.0	-109.4	-14.9
SP17	-103.2	-13.0	-88.7	-11.7	-84.9	-10.9	-92.0	-11.5	-95.2	-11.2	-90.2	-11.1	-90.2	-11.8	-97.9	-12.5	-108.5	-14.7

Table 5. Relative standard deviation (%) of duplicate samples.

Sampling Date	Duplicate	Duplicate Location	Relative Standard Deviation (RSD%)	
			δ^2H	$\delta^{18}O$
6/19/09	A7	Cache la Poudre River	0.1	0.6
6/19/09	A18	SPR at Ovid	0.3	0.1
7/17/09	B6	SPR at Evans	0.1	0.5
7/17/09	B16	SPR at Sterling	0.6	1.0
9/17/09	C12	SPR at Fort Morgan	0.1	0.1
9/17/09	C19	SPR at Julesburg	0.1	0.2
10/22/09	D5	Rd. 60 Above Confluence	0.1	1.4
10/22/09	D17	SPR at Crook	0.04	1.0
1/21/10	E3	SPR at Platteville	0.9	1.8
1/21/10	E12	SPR at Weldona	0.3	0.9
2/23/10	F2	SPR at Henderson	0.3	1.0
2/23/10	F19	SPR at Kersey	0.2	1.1
4/15/10	G4	Big Thompson River	1.2	4.8
4/15/10	G14	SPR at Dodd Bridge Road	0	1.4
5/20/10	H8	SPR at Kersey	0.8	3.2
5/20/10	H15	SPR at Merino	0.2	2.2
6/18/10	I7	Cache la Poudre River	0.1	0.9
6/18/10	I18	SPR at Ovid	0.3	0.3

Table 6. Mean Isotope Compositions and Coefficients of Variation. Mean isotope compositions for all 17 sampling sites and coefficients of variation during all nine sampling rounds during the low (June 2009 to April 2010) and high flow periods (June 2009, May and June 2010).

Sample	Distance (km)	Mean Isotope Compositions (Coefficient of Variation %)		Mean Isotope Compositions during Low Flow		Mean Isotope Compositions during High Flow	
		δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$	δ^2H	$\delta^{18}O$
SP1	0	-110.2 (±4.7)	-14.4 (±5.8)	-108.8 (±5.0)	-14.2 (±6.6)	-113.0 (±3.6)	-14.7 (±3.4)
SP2	32	-107.7 (±3.9)	-13.9 (±3.9)	-105.8 (±2.5)	-13.6 (±2.6)	-111.6 (±4.0)	-14.5 (±1.2)
SP3	47	-110.0 (±5.1)	-14.0 (±7.6)	-107.8 (±3.5)	-13.6 (±4.8)	-114.4 (±6.1)	-15.0 (±8.0)
SP4	44	-109.5 (±4.2)	-14.1 (±4.7)	-106.9 (±2.2)	-13.7 (±2.6)	-114.7 (±2.9)	-14.8 (±2.3)
SP5	55	-109.0 (±4.7)	-14.0 (±5.6)	-106.2 (±2.5)	-13.5 (±3.8)	-114.7 (±3.3)	-14.9 (±0.9)
SP6	58	-110.1 (±8.6)	-14.1 (±10.4)	-104.3 (±3.0)	-13.1 (±5.1)	-121.7 (±4.8)	-15.9 (±0.7)
SP7	68	-109.4 (±5.9)	-14.0 (±6.5)	-105.7 (±2.3)	-13.5 (±4.1)	-117.0 (±3.9)	-15.0 (±1.9)
SP8	70	-98.1 (±4.2)	-12.1 (±8.7)	-97.4 (±5.1)	-12.1 (±9.4)	-99.5 (±8.8)	-12.2 (±8.8)
SP9	84	-79.3 (±7.0)	-8.9 (±13.9)	-78.5 (±8.3)	-8.8 (±16.4)	-80.9 (±9.9)	-9.0 (±9.9)
SP10	123	-103.5 (±7.6)	-13.3 (±12.0)	-98.6 (±1.5)	-12.4 (±4.3)	-113.2 (±4.5)	-15.2 (±9.8)
SP11	135	-103.7 (±15.6)	-13.5 (±18.4)	-92.2 (±15.9)	-12.3 (±14.8)	-112.4 (±4.2)	-15.3 (±10.1)
SP12	144	-102.3 (±7.5)	-13.2 (±9.6)	-97.6 (±2.0)	-12.4 (±3.5)	-111.8 (±4.8)	-14.8 (±4.5)
SP13	177	-98.8 (±6.3)	-12.5 (±8.7)	-95.0 (±2.5)	-11.8 (±4.4)	-106.3 (±3.3)	-13.9 (±1.9)
SP14	201	-100.0 (±7.5)	-13.0 (±10.5)	-95.3 (±1.6)	-12.2 (±3.8)	-109.4 (±4.1)	-14.5 (±8.1)
SP15	242	-97.9 (±7.5)	-12.6 (±11.0)	-93.5 (±2.6)	-11.9 (±5.4)	-106.6 (±5.0)	-14.0 (±10.9)
SP16	279	-95.7 (±7.4)	-12.2 (±10.1)	-91.5(±2.8)	-11.6 (±4.0)	-104.1 (±4.9)	-13.6 (±8.3)
SP17	291	-94.5 (±8.0)	-12.0 (±10.0)	-90.2 (±3.8)	-11.4 (±3.1)	-103.2 (±5.1)	-13.4 (±8.9)

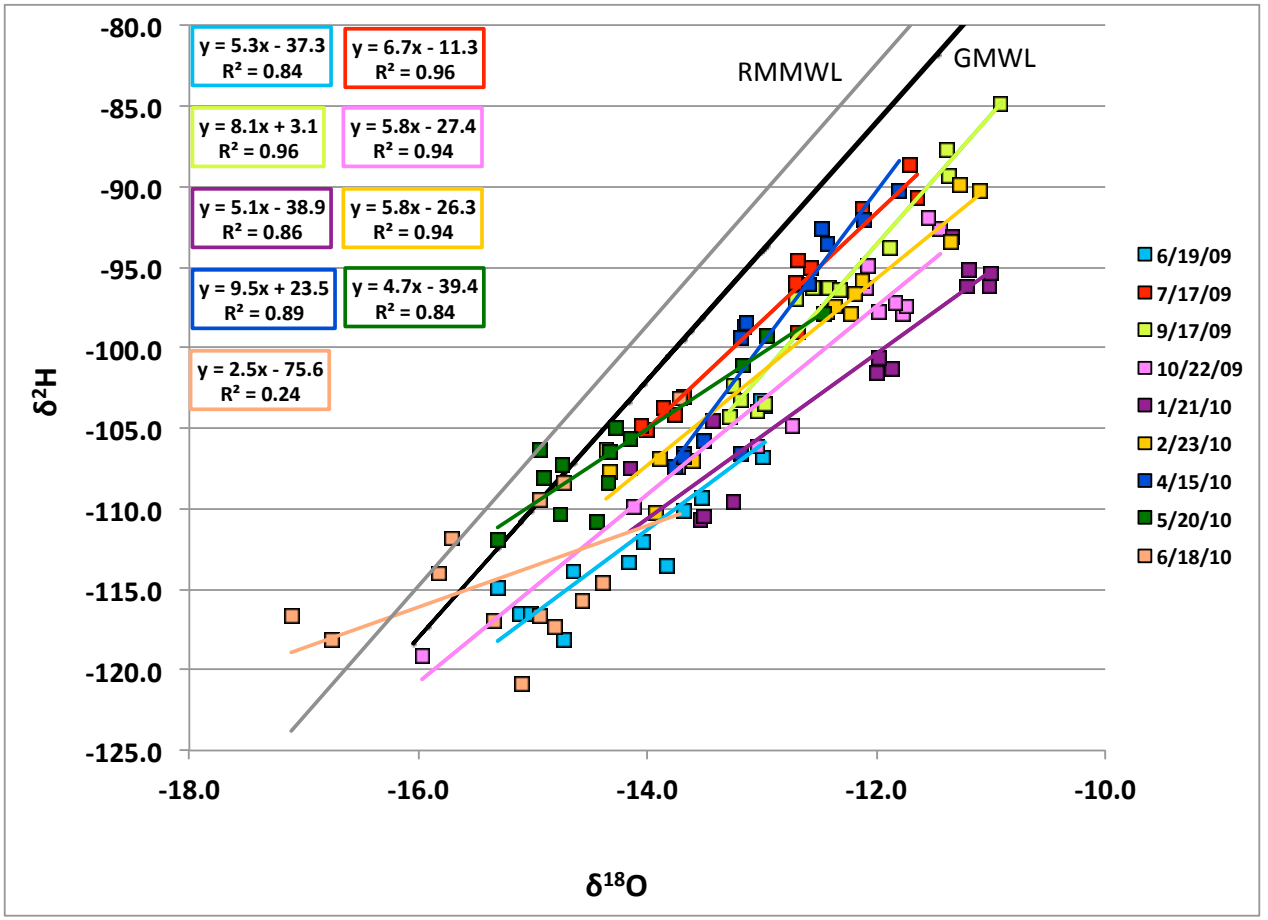

Figure 9. Isotopic signatures of δ^2H and $\delta^{18}O$ of water samples collected at 13 stations along the South Platte River during nine sampling rounds. Shown in gray is the Rocky Mountain Meteoric Water Line ($\delta^2H = 8.1\delta^{18}O + 14.8‰$ SMOW).

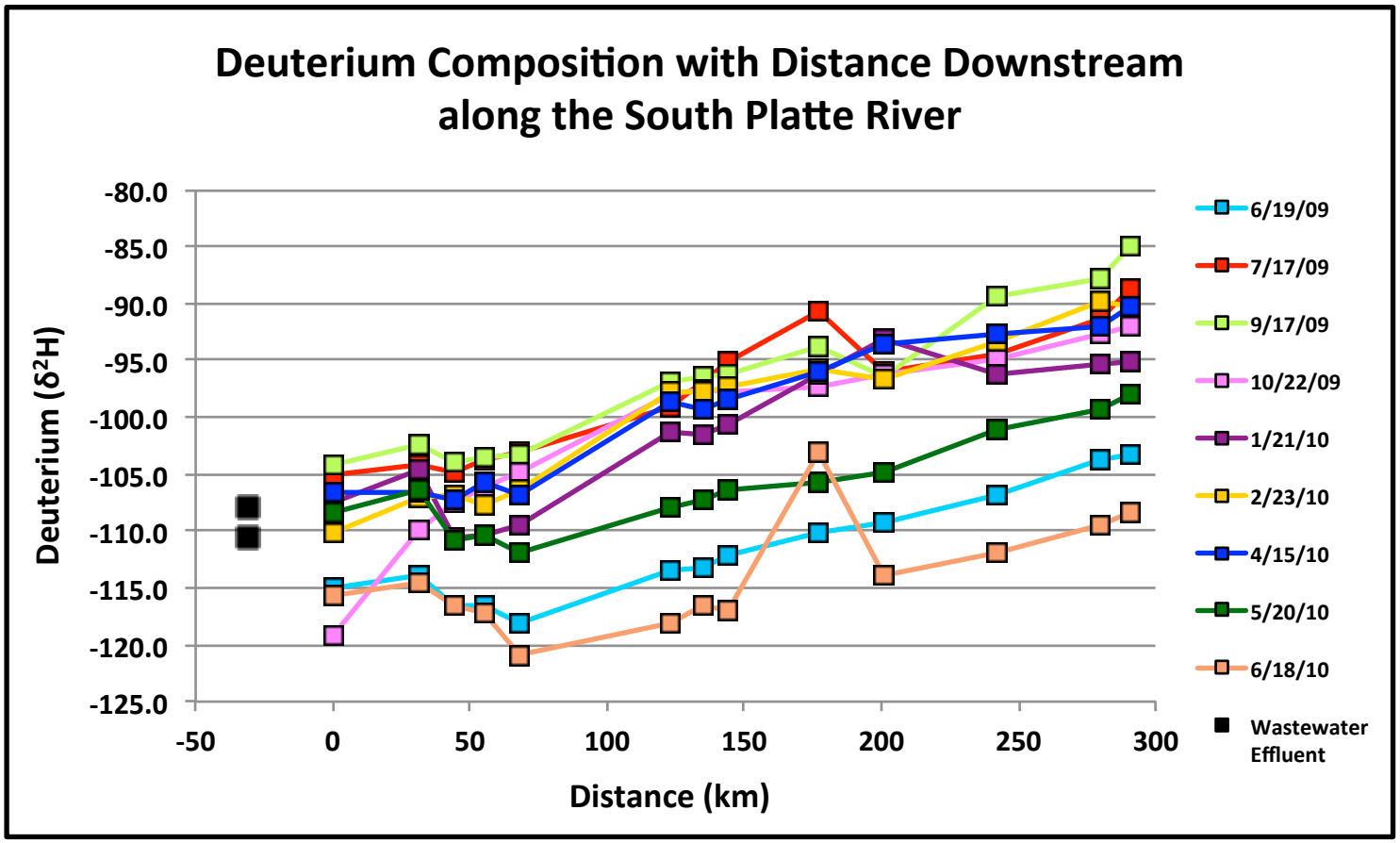

Figure 10. Deuterium compositions with distance downstream within each sampling round along the South Platte River. Shown in black are the isotope compositions of the two samples collected in the wastewater treatment plant at Denver, located ~ 21 kilometers (13 miles) from Henderson on May 2010.

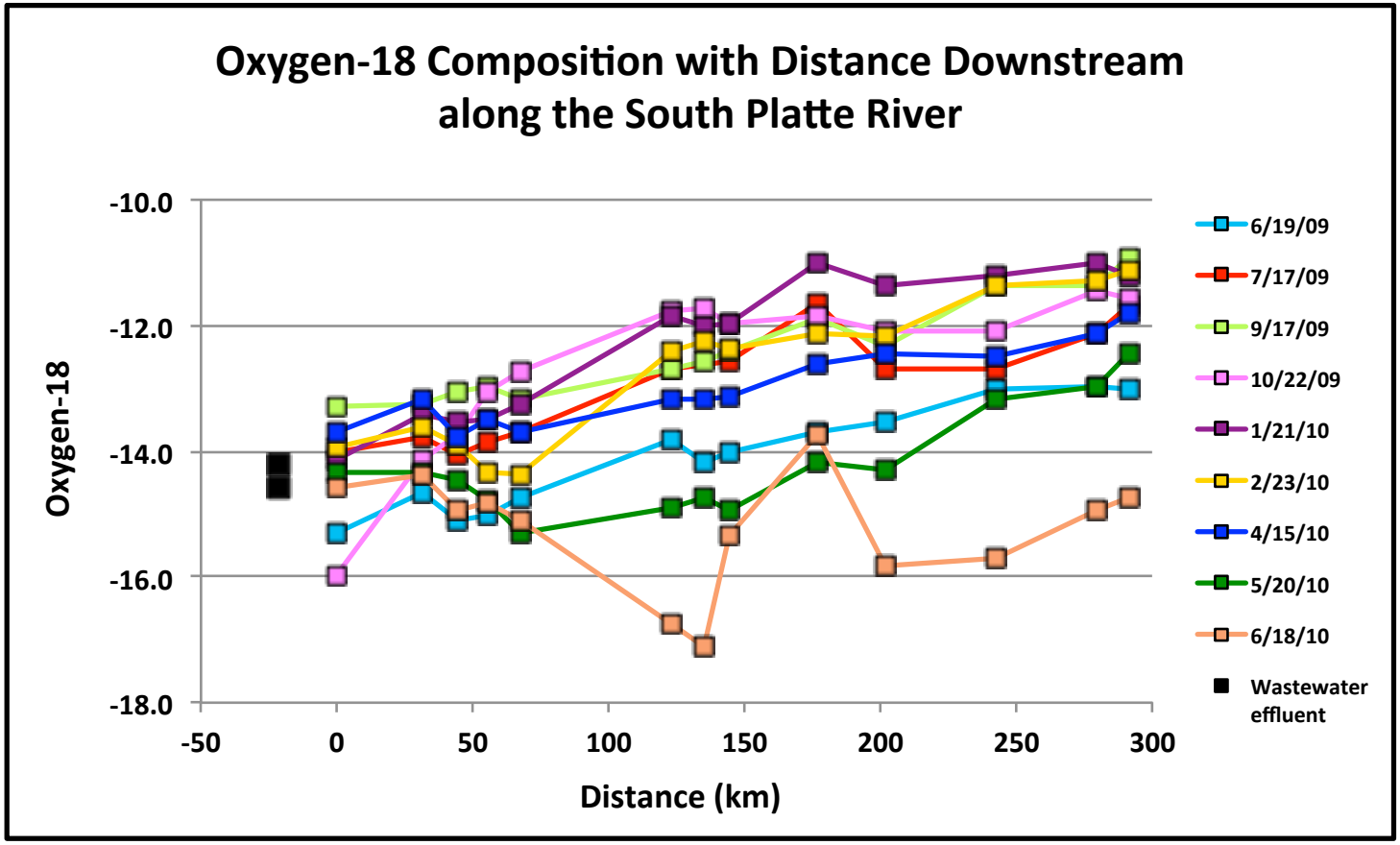

Figure 11. Oxygen-18 compositions with distance downstream within each sampling round along the South Platte River. Shown in black are the isotope compositions of the two samples collected in the wastewater treatment plant at Denver, located ~ 21 kilometers (13 miles) from Henderson on May 2010.

Overall, mean isotope compositions along the South Platte River became enriched with distance downstream from Henderson to Julesburg, with an observed enrichment of + 15 ‰ δ^2H and + 2.3 ‰ $\delta^{18}O$. The mean isotope compositions of tributaries Big Thompson and Cache la Poudre Rivers were similar to those of the South Platte above the confluence with each, yet mean isotope compositions at both Riverside and Jackson Lake Reservoirs were enriched relative to those on the South Platte (Table 6).

4.1.1 Spatial Variations

A spatial linear trend was observed within mean isotope compositions, where these became progressively enriched with distance downstream from Henderson (SP1) (-110.2 ‰ δ^2H and -14.4 ‰ $\delta^{18}O$) downstream towards Julesburg (-94.5 ‰ δ^2H and -12.0 ‰ $\delta^{18}O$). Mean isotope compositions of tributary influx were similar to those of the South Platte River while reservoir water compositions were enriched relative to those along the river (Figure 12 and 13). Mean isotope compositions of the Big Thompson River (SP3) (-110.0 ‰ δ^2H and -14.0 ‰ $\delta^{18}O$) were similar to the compositions of the South Platte River above the confluence (SP4) (-109.5 ‰ δ^2H and -14.1 ‰ $\delta^{18}O$). Still, mean isotope compositions of the Cache la Poudre River (SP6) (-110.1 ‰ δ^2H and -14.1 ‰ $\delta^{18}O$) were also similar to those above the confluence on the South Platte River at Evans (SP5) (-109.0 ‰ δ^2H and -14.0 ‰ $\delta^{18}O$) (Figure 12 and 13). However, mean isotope compositions at both reservoirs, Riverside (SP8) (-98.1 ‰ δ^2H and -12.1 ‰ $\delta^{18}O$) and Jackson Lake Reservoirs (SP9) (-79.3 ‰ δ^2H and -8.9 ‰ $\delta^{18}O$) were enriched relative to isotopic compositions upstream at Kersey (-109.4 ‰ δ^2H and -14.0 ‰ $\delta^{18}O$) (Figure 12 and 13).

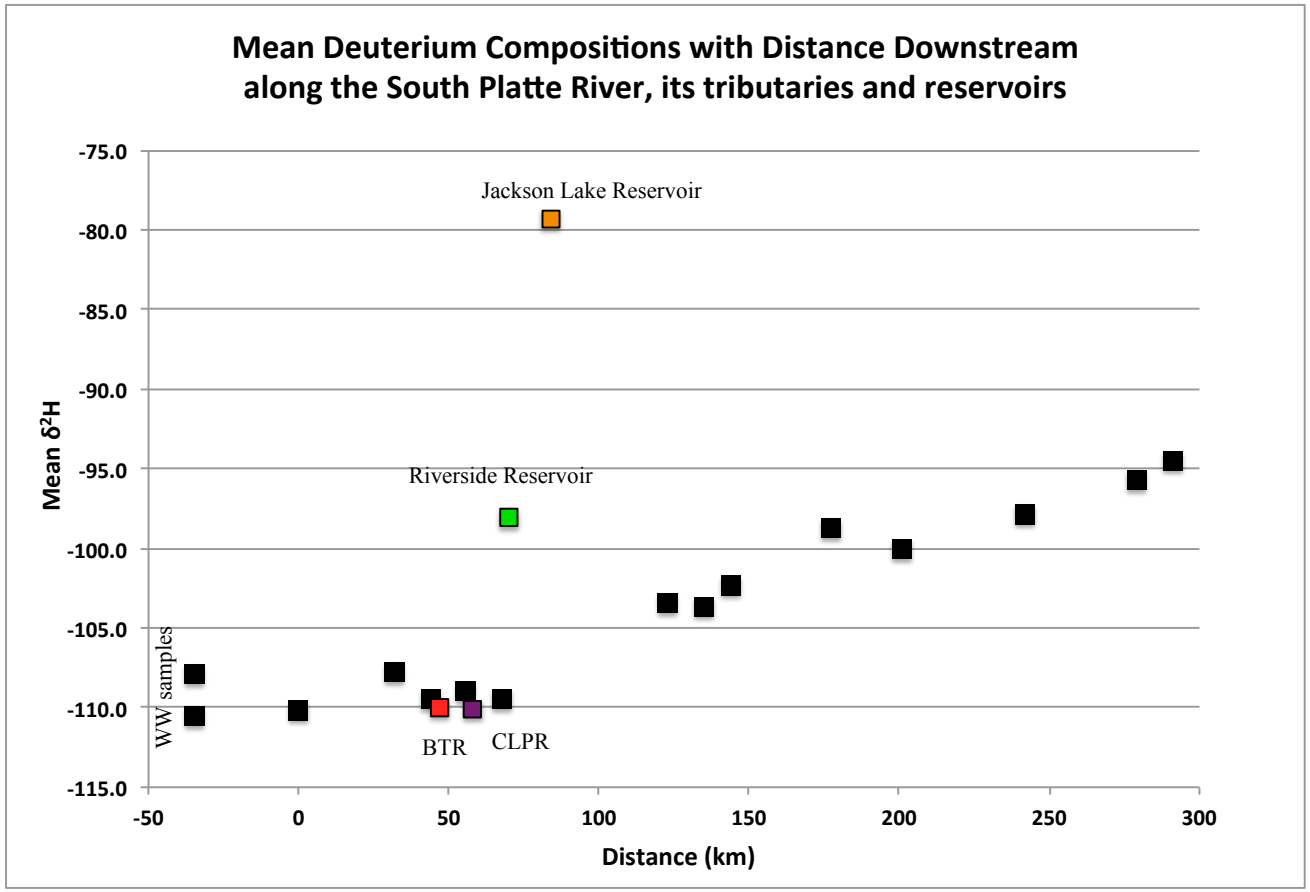

Figure 12. Mean Deuterium Isotope Compositions. General mean isotope composition enrichment was observed with distance downstream along the South Platte River. Isotope compositions for wastewater effluent samples (-35 km) collected on May 2010 were similar to the mean deuterium composition at Henderson.

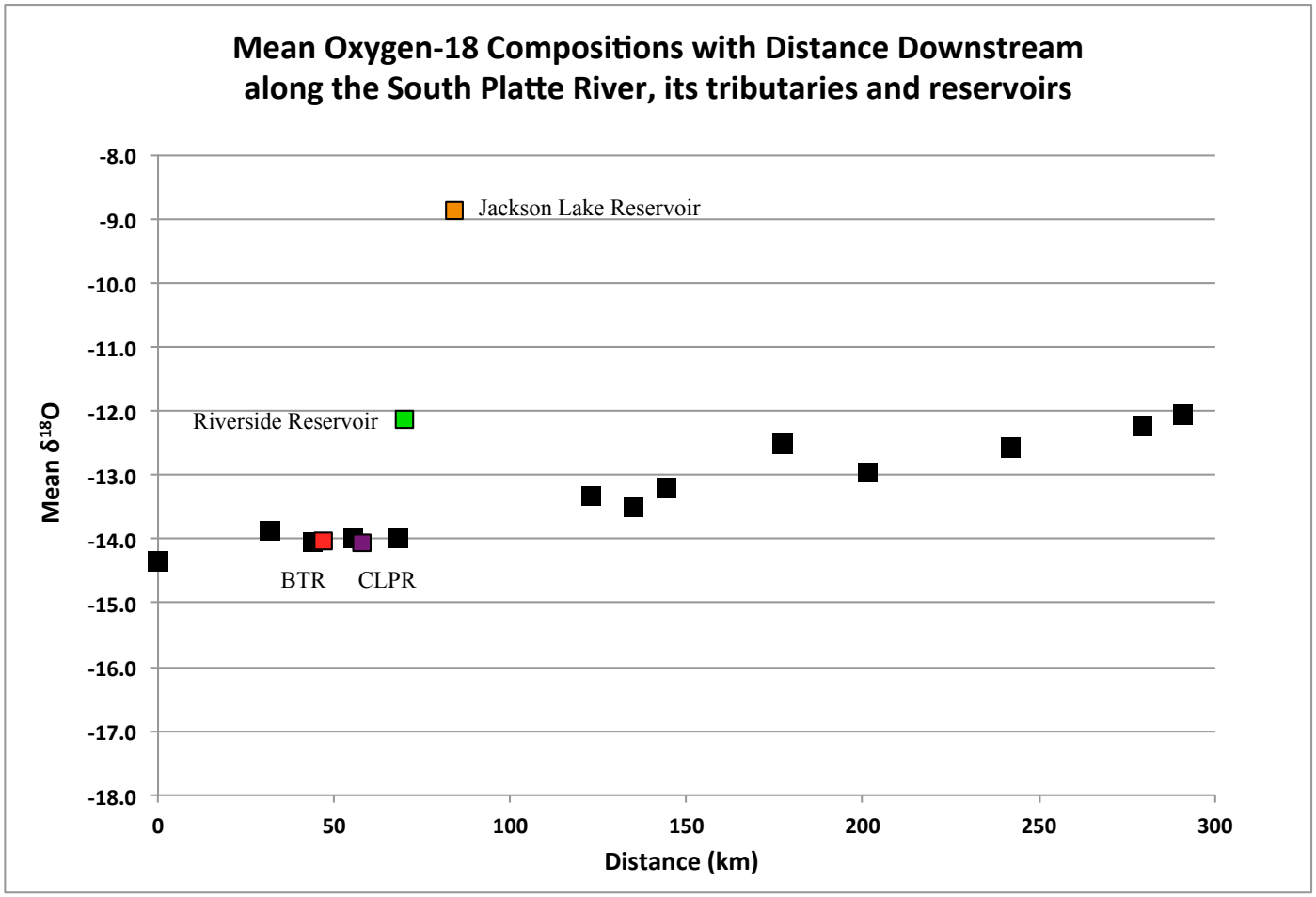

Figure 13. Mean Oxygen-18 Isotope Compositions. General mean isotope composition enrichment was observed with distance downstream along the South Platte River.

Isotope compositions varied differently between sampling sites along the river. Isotope compositions from Henderson to Kersey were less variable than those from Fort Morgan to Julesburg, indicated by lower coefficients of variation (3.9 to 5.9 % δ^2H and 3.9 to 6.5 % $\delta^{18}O$) in the upstream reach of the river (SP1 to SP7) relative to those downstream (6.3 to 15.6 % δ^2H and 8.7 to 18.4 % $\delta^{18}O$) (Table 6). Isotope compositions observed at Fort Morgan were most variable, showed by the highest coefficients of variation of 15.6 % δ^2H and 18.4 % $\delta^{18}O$.

4.1.2 Temporal Variations

Isotope compositions of the South Platte River were different within the various seasonal periods. Mean stable isotope compositions were generally enriched during the fall (September and October) (-98.9 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$) and winter (January and February) (-100.7 ‰ δ^2H and -12.5 ‰$\delta^{18}O$) seasons of 2009-2010 relative to those during the summer (June and July) (-104.8 ‰ δ^2H and -13.5 ‰ $\delta^{18}O$) of 2009 and the spring (April and May) (-102.8 ‰ δ^2H and -13.6 ‰ $\delta^{18}O$) and summer (June) (-114.1 ‰ δ^2H and -15.2 ‰ $\delta^{18}O$) seasons of 2010 (Figures 14, 15, 16 and 17).

4.1.3 Discharge along the South Platte River in 2009-2010

Mean enriched isotope compositions were predominant during the low flow period (-99.5 ‰ δ^2H and -12.8 ‰ $\delta^{18}O$), from July 2009 to April 2010, relative to mean depleted isotope compositions during the high flow period (-110.1 ‰ δ^2H and -14.3 ‰ $\delta^{18}O$) in June 2009, May and June 2010 (Table 6 and Figures 10, 11, 14 and 15).

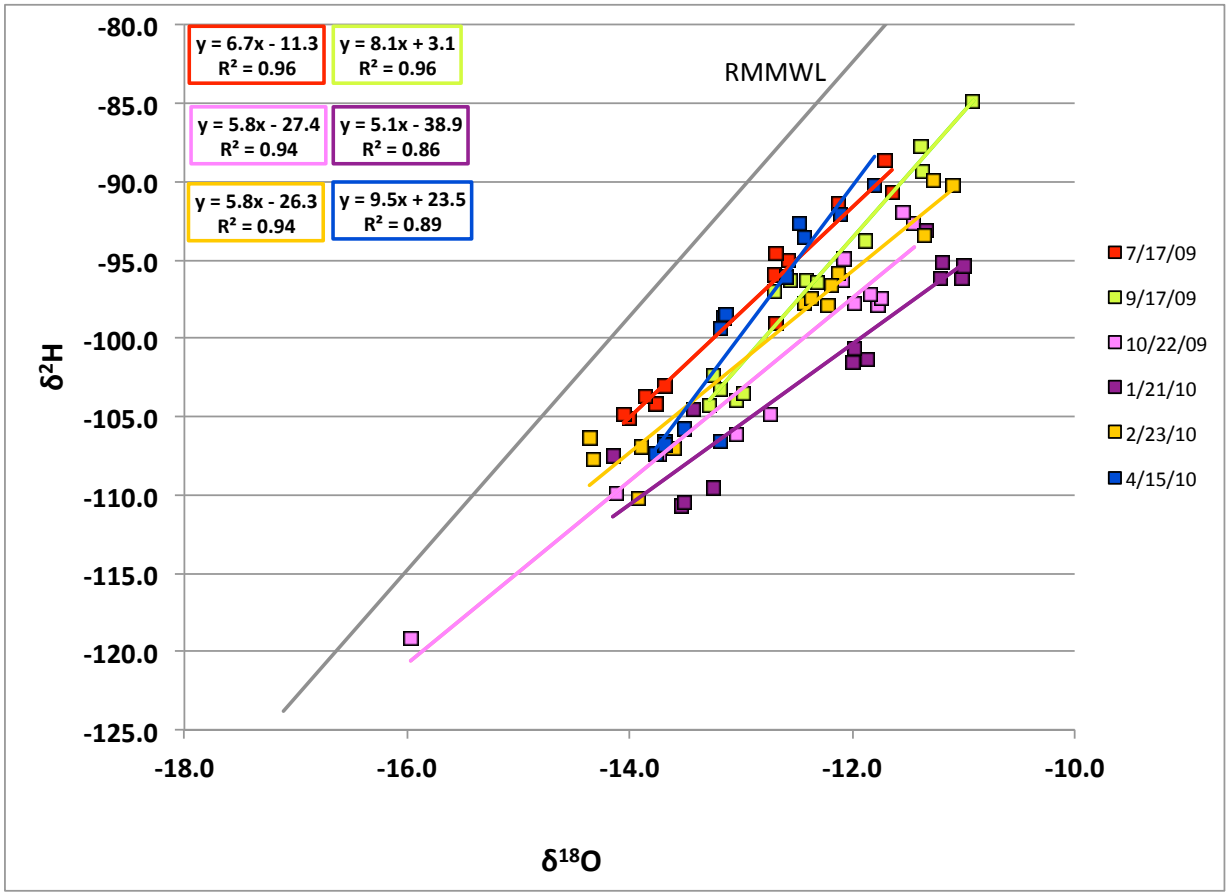

Figure 14. Isotope Signatures along the South Platte River during the low flow period. Isotopic signatures of δ^2H and $\delta^{18}O$ of water samples collected at 13 stations along the South Platte River during the low flow period (July 2009 to April 2010). Shown in gray is the Rocky Mountain Meteoric Water Line ($\delta^2H = 8.1\delta^{18}O + 14.8‰$ SMOW).

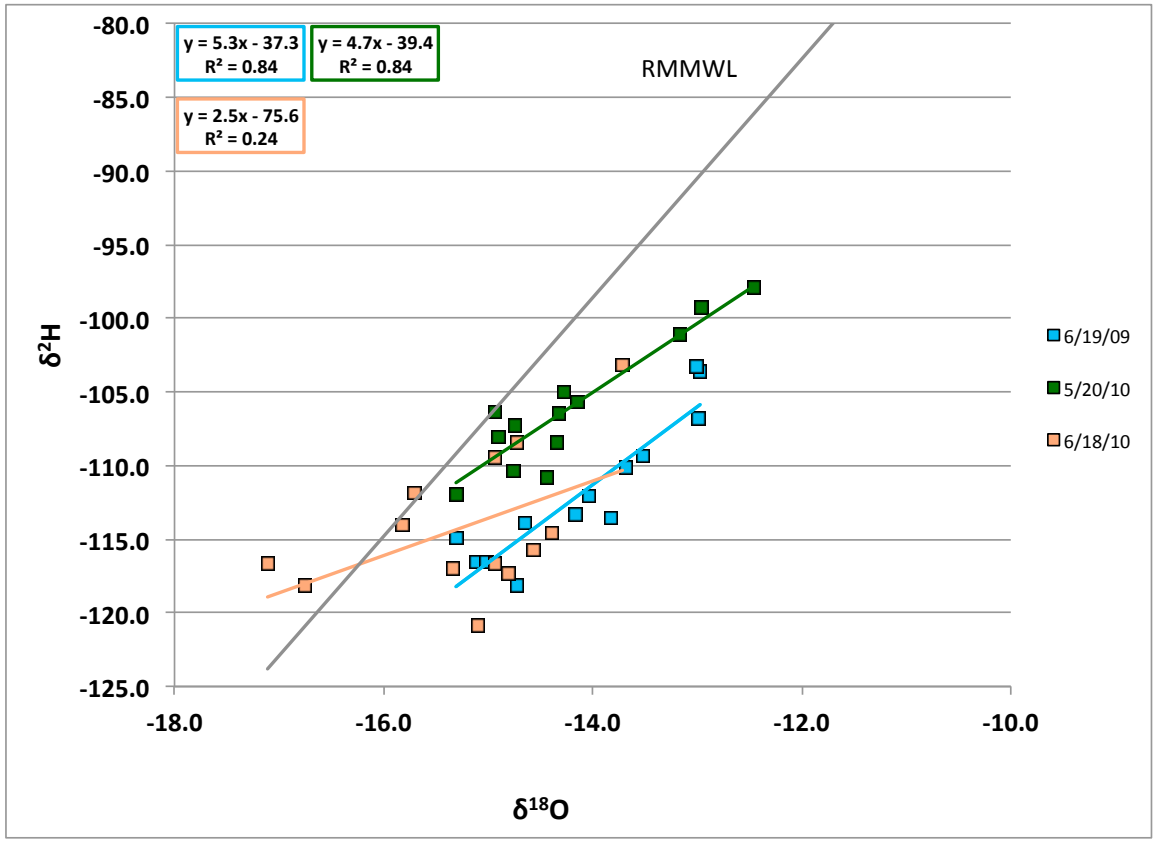

Figure 15. Isotope Signatures along the South Platte River during the high flow period. Isotopic signatures of δ^2H and $\delta^{18}O$ of water samples collected at 13 stations along the South Platte River during the high flow period (June 2009, May 2010 and June 2010). Shown in gray is the Rocky Mountain Meteoric Water Line ($\delta^2H = 8.1\delta^{18}O + 14.8‰$ SMOW).

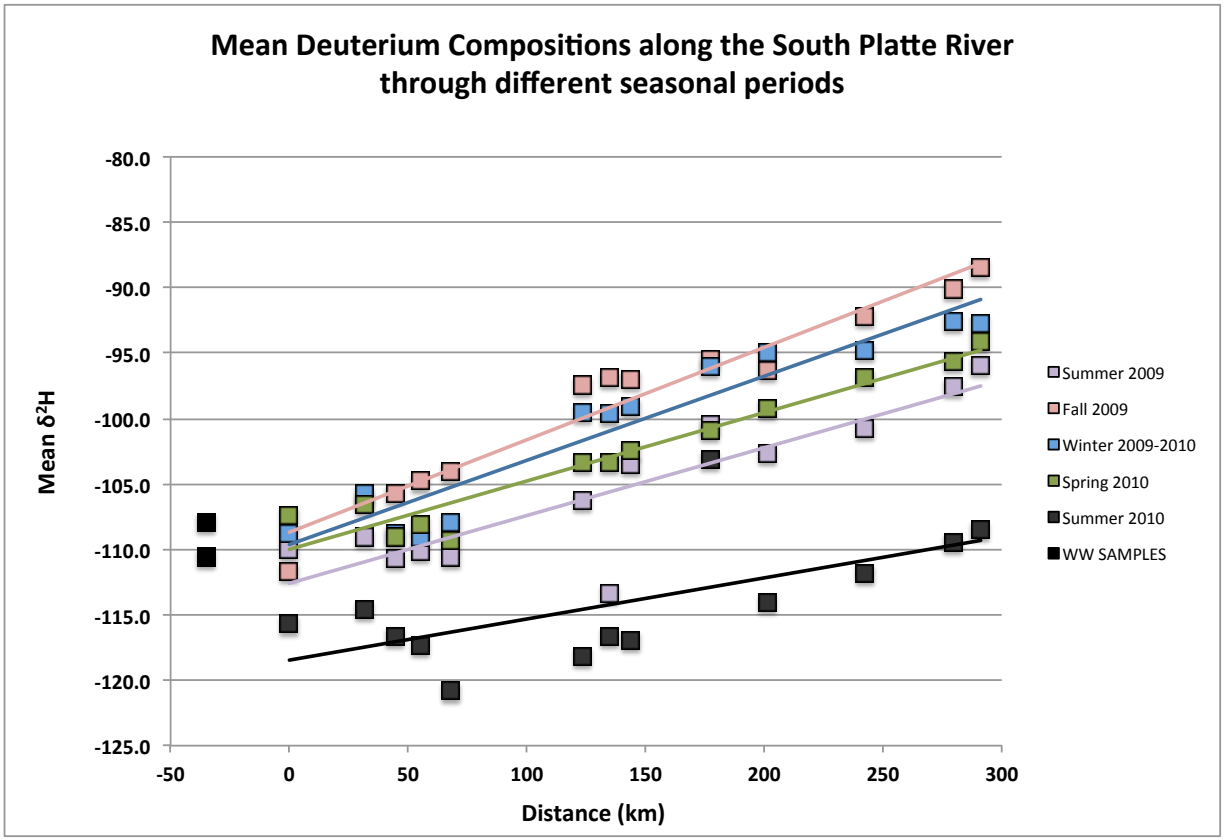

Figure 16. Mean deuterium compositions along the South Platte River through different seasonal periods. A change in isotope compositions was observed with distance downstream with a general defined linear enrichment during five seasonal periods sampled on 2009 – 2010. Stable isotope compositions of wastewater samples (-35 km) collected on May 2010 showed similar isotope compositions to those at Henderson on summer 2009, fall 2009, winter 2009 – 2010 and spring 2010.

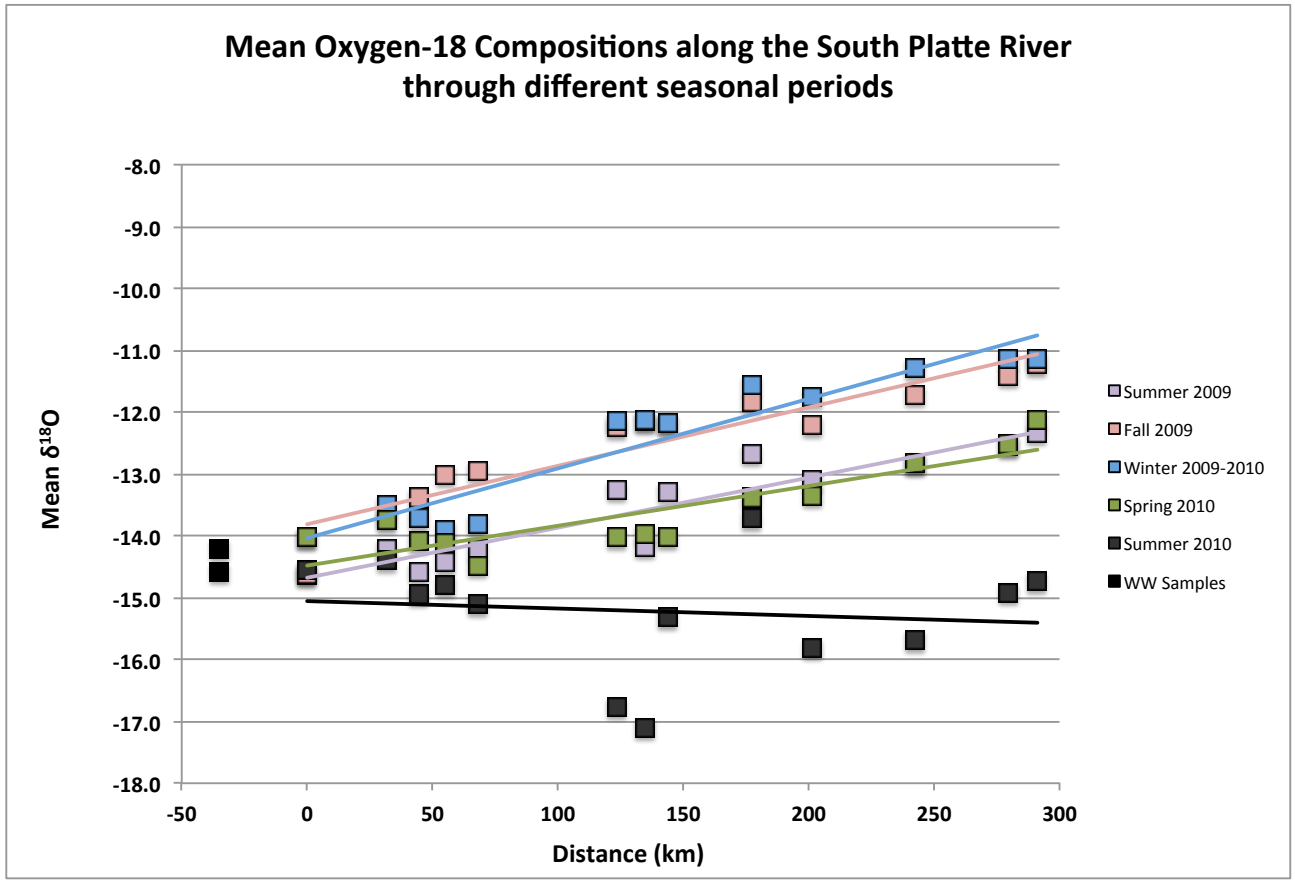

Figure 17. Mean oxygen-18 compositions along the South Platte River through different seasonal periods. A change in oxygen-18 was observed with distance downstream with a general defined linear enrichment during five seasonal periods sampled on 2009 – 2010.

Even though mean isotope compositions of the Big Thompson River and the Cache la Poudre River were similar to those of the South Platte above each confluence during the one-year sampling period, a slight difference was observed in isotope compositions of tributaries during the different flow levels relative to those above each confluence in the South Platte River. During the low flow period, mean isotope composition of δ^2H at the Big Thompson River (-107.8 ‰ δ^2H) was depleted relative to that above the confluence at the South Platte River (-106.9 ‰ δ^2H), while the mean isotope composition at Cache la Poudre River (-104.3 ‰ δ^2H) was enriched relative to the mean deuterium composition above the confluence at Evans (-106.2 ‰ δ^2H) (Figure 18).

Mean isotope compositions of δ^2H at both Riverside (-97.4 ‰ δ^2H) and Jackson Lake (-78.5 ‰ δ^2H) Reservoirs were noticeably enriched relative to that at Kersey (-105.7 ‰ δ^2H) (Figure 18). During the high flow period, the mean isotope composition of δ^2H at the Big Thompson River (-114.7 ‰ δ^2H) was similar to that above the confluence at the river (-78.5 ‰ δ^2H), but the mean isotope composition was significantly depleted at the Cache la Poudre River (-121.7 ‰ δ^2H) relative to that upstream at Evans (-114.7 ‰ δ^2H) (Figure 19). However, mean isotope composition of Riverside (-99.5 ‰ δ^2H) and Jackson Lake Reservoirs (-80.9 ‰ δ^2H) were also enriched during the high flow period in comparison to that upstream at Kersey (-117.0 ‰ δ^2H) (Figure 19).

4.2 Experimental Lines

A distinct enrichment in isotope compositions was observed in sampling sites with distance traveled downstream within every experimental line (except June 2010) (Figure 9). Slope values for every sampling period line during the high flow period were lower (less positive) relative to those from the low flow period, however most of the slope values were less than the slope of the GMWL (8.0). The slope of the experimental line of September 2009 (8.1) and April 2010 (9.5) exceeded that of the GMWL (Table 7 and Figure 9) but most of the lines showed slopes pertaining to that characteristic of evaporation lines (4 to 7), except the lowest slope (2.5) observed in June 2010 (Table 7). The line for June 2010 showed high variability on the isotope compositions of samples and these were poorly correlated within this round ($r^2 = 0.24$).

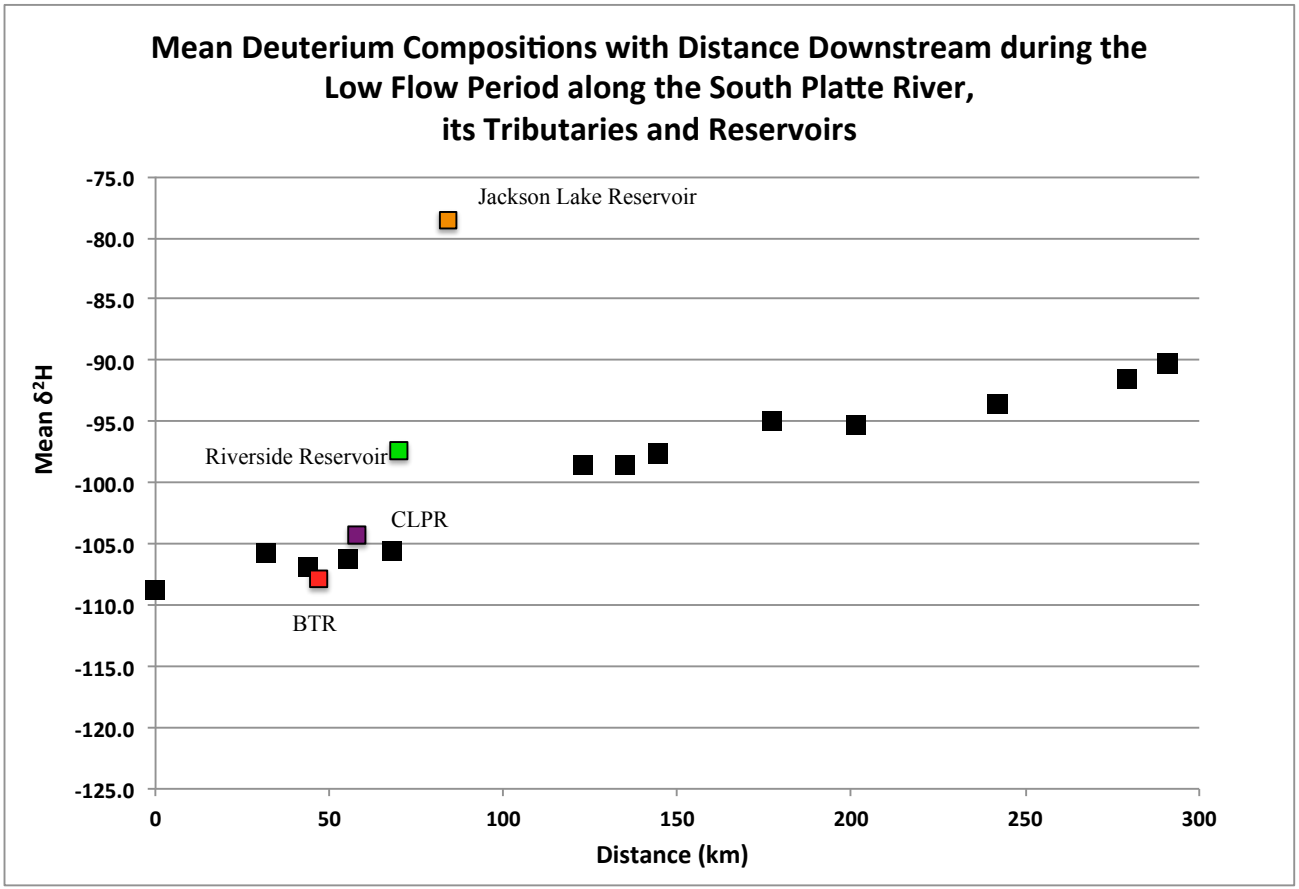

Figure 18. Mean Deuterium Isotope Compositions during the low flow period.

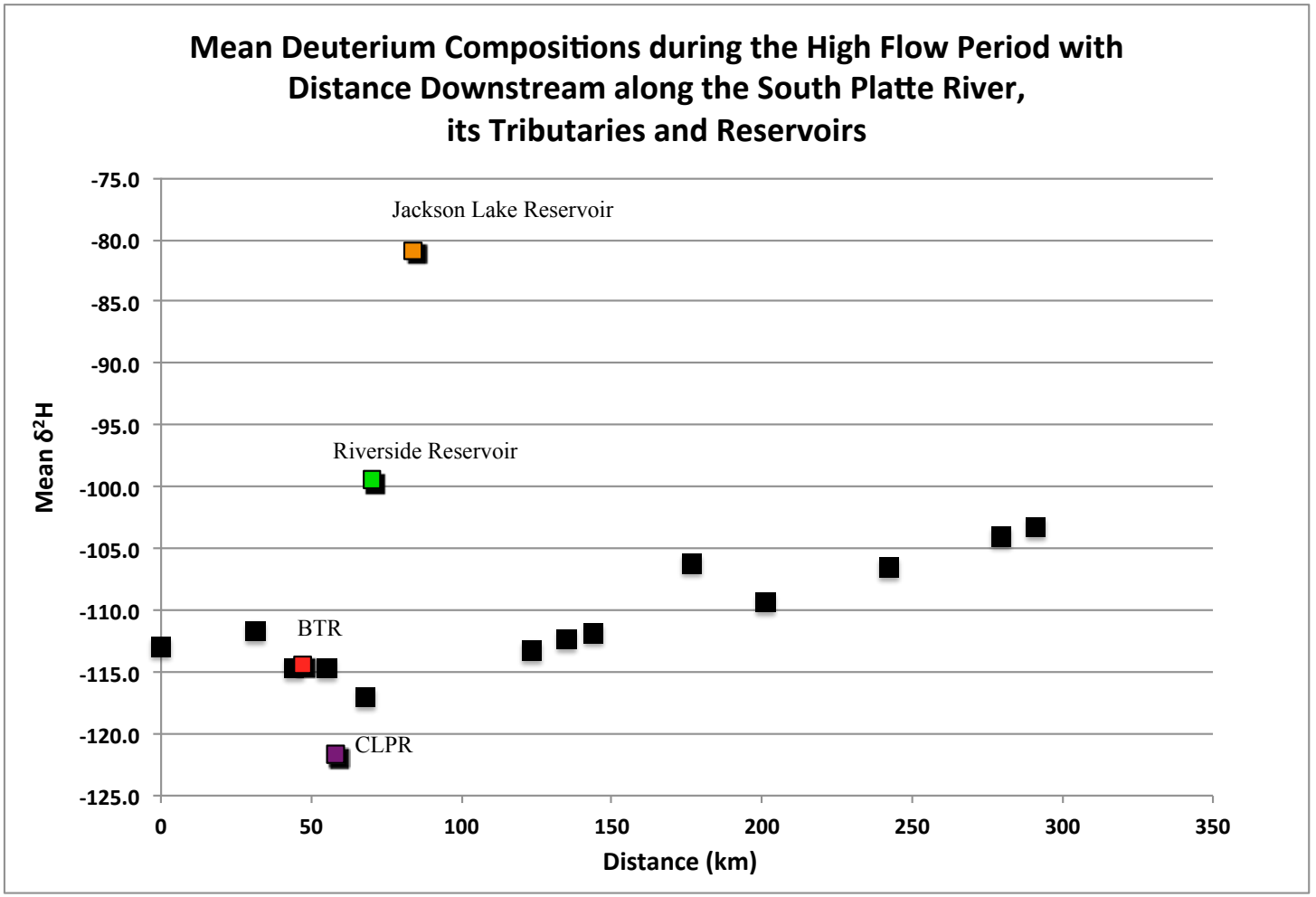

Figure 19. Mean Deuterium Isotope Compositions during the high flow period.

Table 7. Evaporation line equations for all sampling rounds, best fit of the line (R^2) and daily discharge at Fort Morgan on sampling dates.

Sampling Date	Regression Line	R^2	Discharge (ft^3/s)
6/19/09	y = 5.3x - 37.3	0.84	2770
7/17/09	y = 7.4x - 2.1	0.99	187
9/17/09	y = 8.1x + 3.1	0.96	232
10/22/09	y = 5.8x - 27.4	0.94	289
1/21/10	y = 5.1x - 38.9	0.86	338
2/23/10	y = 5.8x - 26.3	0.94	138
4/15/10	y = 9.5x + 23.5	0.89	123
5/20/10	y = 4.7x - 39.4	0.84	3150
6/18/10	y = 2.5x - 75.6	0.24	8650

Chapter 5

DISCUSSION

Stable isotope compositions (except two sampling points on June 2010) along the South Platte River plotted below the Rocky Mountain Meteoric Water Line ($\delta^2H = 8.1\ \delta^{18}O + 14.8‰$ SMOW) [A. Mast, personal communication], meaning the isotope compositions of river water were different than the isotope compositions of the meteoric water line which are based on precipitation at the regional scale (Figure 9). Isotope compositions of local precipitation changes through space and time as isotopes are fractionated differently by evaporation processes that affect rainfall below the cloud base and by the compositions of the different vapor sources generating precipitation amongst others [Araguas – Araguas et al., 2000]. Similarly, evaporation processes and the contributions of sources of water with different origins characterized by particular isotope signatures also affect the overall isotope compositions in a river system. This chapter discusses stable isotope compositions of the South Platte River, how these changed spatially, temporally and during different flow periods and the processes that might have caused these changes.

5.1 Spatial Variations along the South Platte River

Stable isotope compositions along the South Platte River, with increasing distance from Henderson (SP1) to Julesburg (SP17), plotted in a general linear enrichment tendency within all of the sampling rounds (Figure 10 and 11), with depleted mean isotope compositions at Henderson (-110.2‰ δ^2H and -14.4‰ $\delta^{18}O$) relative to the mean compositions at Julesburg (-94.5‰ δ^2H and -12.0‰ $\delta^{18}O$). Enrichment in sable isotope compositions along the river could have occurred by the effect of evaporation processes on surface water that caused enrichment in the heavy isotope forms with distance downstream, by the contribution of enriched sources of water to the river or by a combination of these. On perennial rivers located in arid regions, headwaters are localized at a higher elevation where temperature is typically lower than the rest of the arid catchment area (downstream), reflecting colder water less subject to evaporation at the headwaters than in the rest of the arid catchment [Araguas-Araguas et al., 2000; Kendall and McDonnell, 1998]. The more time water has spent in the river channel, the more subject to evaporation it has been and the lighter isotope forms of water have been transformed to the vapor phase, concentrating the heavier isotope forms (δ^2H and $\delta^{18}O$) in the remaining river water. Besides evaporation, the enrichment in isotope compositions downstream might have occurred as a cumulative effect of enriched tributary and reservoir influx water sources that have discharged along the river.

The variation observed in mean isotope compositions from Henderson to Kersey was not significant, indicated by coefficients of variation, even though a slight enrichment was still observed with distance downstream (Figure 10 and 11 and Table 6). Due to the small change in compositions, it is likely that there was just one source of

water that dominated discharge along this reach of the river and the minimal enrichment in heavy isotope forms occurred mainly from evaporation processes. The discharge produced by wastewater effluent from Denver and the Front Range in Colorado comprises ~ 90% of the flow in the river during 9 months, even though the direct effect of wastewater discharge is not distinguishable more than 48 kilometers (30 miles) downstream [Harris, 1993; Camp Dresser and McKee, 1994; Dennehy et al., 1998; Sprague, 2005]. During most of the sampling rounds, the mean isotope compositions at Henderson were similar to those of the wastewater effluent (-110.5 ‰, -107.9 ‰ δ^2H and -14.6 ‰, -14.2 ‰ $\delta^{18}O$), suggesting this could be the main contributing source of water in this reach of the river even though the possibility of other contributing sources of water (e.g. urban runoff, diversions, reservoirs, irrigation return flows) still exists.

From Kersey to Julesburg, coefficients of variation were higher than those upstream indicating the change stable isotope compositions was greater and more pronounced also seen and indicated by the clear enrichment observed with distance downstream. This behavior suggests that more than one source of water with different isotope signatures contributed discharge along this reach of the river as well as evaporation processes that caused enrichment in the heavier isotope forms of water. Besides wastewater effluent, other sources of water not identified in this study such as irrigation return flows, urban and agricultural runoff, diversions and storage water possibly contributed considerable amounts of discharge to the South Platte. From Kersey to Julesburg, agricultural land dominates the land use highly suggesting irrigation return flows, agricultural runoff and any other source of water related to agricultural practices are main contributing components with particular isotope signatures that affect those of

river water. Isotope compositions of irrigation return flows, agricultural runoff, diversions and storage water need to be known in order to identify these as sources of water that have an effect on the South Platte River, which is beyond the scope of this study.

5.1.1 Tributaries and Reservoirs

The effect mean isotopic composition of tributary river water discharged into the South Platte River was not significant as compositions at the river above and below the confluences were similar (Table 6). Isotope compositions of both the Big Thompson River (-110.0 ‰ δ^2H and -14.0 ‰ $\delta^{18}O$) and the Cache la Poudre River (-110.1 ‰ δ^2H and -14.1 ‰ $\delta^{18}O$) were similar to those in the South Platte above the confluences (Table 6 and Figure 12 and 13). Similar isotope compositions below the confluence at Evans (SP5) (-109.0‰ δ^2H and -14.0‰ $\delta^{18}O$) and above the confluence (SP4) (-109.5‰ δ^2H and -14.1‰ $\delta^{18}O$) demonstrated the effect isotopic compositions of the Big Thompson River (-110.0‰ δ^2H and -14.0‰ $\delta^{18}O$) had on the South Platte River was not significant. Isotope compositions discharged from the Cache la Poudre River (-110.1‰ δ^2H and -14.1‰ $\delta^{18}O$) did not have a significant effect on the South Platte River water as well due to the similarity in compositions below the confluence at Kersey (SP7 (-109.4‰ δ^2H and -14.0‰ $\delta^{18}O$) relative to those upstream at Evans (SP5) (-109.0‰ δ^2H and -14.0‰ $\delta^{18}O$) (Figure 12 and 13).

The enrichment observed in mean isotopic compositions from Kersey (-109.4‰ δ^2H and -14.0‰ $\delta^{18}O$) to Weldona (SP10) (-103.5‰ δ^2H and -13.3‰ $\delta^{18}O$), indicated that besides evaporation causing enrichment downstream, discharge of enriched water

from Riverside (-98.1‰ δ^2H and -12.1‰ $\delta^{18}O$) and Jackson Lake (-79.3‰ δ^2H and -8.9‰ $\delta^{18}O$) Reservoirs might have contributed to the overall enrichment observed downstream. The effect these enriched waters had on the South Platte River is not clearly understood as the exact locations water from both these reservoirs discharged into the river are not known.

Mean isotope compositions of both reservoirs show significant enrichment (Figure 12 and 13) since water in lakes and reservoirs is stored for longer periods of time and experience more evaporation an thus enrichment relative to river water [Kattan, 2007]. Riverside Reservoir has a maximum storage of ~65,000 acre-feet and Jackson Lake Reservoir has a maximum storage of 35,629 acre-feet, meaning Riverside Reservoir has the capacity to store more water [The Wilson Bulletin, 1963; Sobieski and Wilson, 2004]. In 1995, residence time for both reservoirs was determined and the maximum residence time for Jackson Reservoir (560 days) was higher than that of Riverside Reservoir (332 days), meaning water spent more time stored in Jackson Reservoir (Sprague, 2002). Because water is stored longer at Jackson Lake Reservoir, it is subject to evaporation for a longer period of time and thus yielded enriched mean isotope compositions (-79.3‰ δ^2H and -8.9‰ $\delta^{18}O$) relative to those at Riverside Reservoir (-98.1‰ δ^2H and -12.1‰ $\delta^{18}O$). The difference in enrichment of both reservoirs reflects the effect evaporation has on isotope compositions and how enrichment occurred as a result of this kinetic process.

5.2 Temporal Variations

Rivers are highly affected by seasonal changes depending on their location and topography. The mean isotope compositions during the summer (June and July) of 2009 (-104.8 ‰ δ^2H and -13.5 ‰ $\delta^{18}O$) were depleted relative to those during the fall (September and October) of 2009 (-98.9 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$), indicating that from summer to fall already evaporated sources of water with enriched isotopic compositions possibly dominated discharge during this period (Figure16 and 17). When evaporation occurs in a surface water body, fractionation processes transform the lighter isotope forms first into the vapor phase, thus enriching the remaining water in the river in deuterium and ^{18}O compositions [Mazor, 2004]. The highest mean temperature through the study occurred in July 2009 (23 ^oC), contributing to higher rates of evaporation. During the fall season the irrigation season on the northeastern part of the basin is close to an end, indicating a change in river water usage and contributing sources of water occurred. Throughout the irrigation season, storage, reservoirs and diversions have a significant impact on river water as these control river flow in order to supply this limited resource for agriculture and drinking water. When the irrigation season ends during the fall and winter seasons, storage reservoirs start filling and flow in the river is low as precipitation is mainly received as snow and water tables are low since small amounts of water are being infiltrated (Sprague, 2002).

Mean isotope compositions in the winter of (January and February) 2009-2010 (-100.7 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$), were similar to those during the fall of 2009 (-98.9 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$), indicating that even though water might have previously been affected by evaporation, water sources discharging into the river during the fall and

winter were isotopically similar or the water source might have been only one (Figure 16 and 17). During the winter, isotope compositions observed at Henderson (-110.2 ‰, -107.4 ‰ δ^2H and -14.1 ‰, -13.9 ‰ $\delta^{18}O$) were very similar to those of the wastewater treatment plant in Denver (-110.5 ‰ and -107.9 ‰ δ^2H and -14.6 ‰ and -14.2 ‰ $\delta^{18}O$) located 21 kilometers (13 miles) upstream of this initial site, suggesting wastewater effluent discharged at Denver could possibly be a contributing source of water to the river through this period (Figure 10 and 11).

Mean isotope compositions during the spring (April and May) of 2010 (-111.9 ‰ to -90.2 ‰ δ^2H and -17.1 ‰ to -12.5 ‰ $\delta^{18}O$) were depleted relative to those during the winter (January and February) of 2009-2010 (-100.7 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$), indicating an isotopically depleted water source discharged into the river (Figure 16 and 17). In the spring, the discharge levels along the South Platte River increased considerably as high volumes of water were contributed by snowmelt from the Central Rocky Mountains [Sprague, 2005] (Table 3, Figure 8, 16 and 17). In the summer (June) of 2010, mean isotope compositions were the most depleted relative to all other seasons, suggesting the high discharge of isotopically depleted snowmelt received from the Central Colorado Mountains mainly drove streamflow along the South Platte River during this period.

In June of 2010, isotope compositions generally became linearly enriched with distance downstream similar to the other sampling rounds with the exception of isotope composition of δ^2H at Merino (-103.1 ‰) which showed an unexpected enrichment peak (Figure 10). During this round, $\delta^{18}O$ compositions at Weldona, Fort Morgan, Dodd Bridge Road and Merino also caused the linear enrichment observed in all other rounds to

be disrupted (Figure 11). These noticeable changes in stable isotope compositions at these locations relative to the other locations along the South Platte suggest singular sources of water with particular isotope compositions were directly discharged at these locations. Also, there is a possibility that water consisting the water sample was not well mixed and the isotope compositions observed only characterized that particular single source of water.

5.3 Discharge Variations

Discharge levels in the South Platte River during the study period were noticeably divided in two groups: the low flow (from July 2009 to April 2010) and the high flow (June 2009, May and June 2010) (Table 6, Figure 18 and 19). Overall, stable isotope compositions during the low flow period along the South Platte (-99.5 ‰ δ^2H and -12.8 ‰ $\delta^{18}O$) were enriched relative to those during the high flow period (-110.1 ‰ δ^2H and -14.3 ‰ $\delta^{18}O$) (Table 6 and Figures 18 and 19). During the high flow period, discharge increased as a result of snowmelt characterized by depleted isotope compositions (Table 3 and Figure 8). Discharge levels at Fort Morgan ranged from 120 to 340 ft^3/s during the low flow period compared to the high flow period where they ranged from ~ 2800 to more than 8000 ft^3/s, which caused isotopic compositions during this time to be affected to a higher extent by isotopially depleted (Table 3 and Figure 8).

A change in mean isotope compositions was also observed in the Big Thompson and Cache la Poudre Rivers through the different discharge periods. During the low flow period, the mean isotope compositions at the Cache la Poudre River (-104.3 ‰ δ^2H and -13.1 ‰ $\delta^{18}O$) were enriched relative to those upstream at Evans (-106.2 ‰ δ^2H and -13.5 ‰ $\delta^{18}O$), causing a general enrichment at Kersey (-105.7 ‰ δ^2H and -13.5 ‰

$\delta^{18}O$). During the high flow period, the opposite behavior occurred as mean isotope compositions at the Cache la Poudre River (-121.7 ‰ $\delta^{2}H$ and -15.9 ‰ $\delta^{18}O$) were depleted relative to those upstream at Evans (-114.7 ‰ $\delta^{2}H$ and -14.9 ‰ $\delta^{18}O$), causing a general depletion in compositions downstream at Kersey (-117.0 ‰ $\delta^{2}H$ and -15.0 ‰ $\delta^{18}O$).

5.4 Slopes of Experimental Lines

The slopes (2.5 – 9.5) of all nine experimental lines deviated from that of the RMMWL (8.1), except on September 2009 when the slope of the line was equal to that of the local meteoric water line (Table 7 and Figure 9). The deviation of slopes of experimental lines was variable between every sampling round. Isotope compositions along the South Platte River lie below those of the GMWL and RMMWL, indicating these were partitioned under different conditions (e.g., relative humidity, temperature, vapor sources, evaporation) than those conditions under which isotope compositions of the meteoric water lines formed [Benson, 1994; Araguas-Araguas et al., 2000]. Changes in isotope compositions along the river within every sampling period could have also been affected by the contribution of different origin vapor sources that change during seasons and contribute precipitation with distinctive isotope compositions [Benson, 1994; Araguas-Araguas et al., 2000]. Through the diverse seasons, the principal and crucial vapor sources contributing and driving precipitation in the plains area of the South Platte River Basin are diverse: during the summer, convective storms are the main vapor source; while in the winter, storms transported from the east of the United States are the

principal precipitation source whereas during the spring, the key vapor source arises from the Gulf of Mexico moisture [Saunders III and Lewis Jr., 2003].

Throughout the seasonal periods, the different isotope compositions observed within each sampling round could be attributed to changes in the characteristic compositions of each vapor source besides the different isotope signatures contributed by the different sources of water that discharged into the river. In the winter, experimental lines in the summer 2009, late fall (October) 2009, winter 2009 – 2010 and late spring (May) 2010 had slope values ranging from 4.7 to 6.7, indicating evaporation processes took place and affected and caused fractionation in rainfall, snowfall, irrigation return flows, groundwater and agricultural/urban runoff that might have contributed discharge [Bowen, 1986; Kendall and McDonnell, 1998; Horst et al., 2007; Kattan, 2007].

Chapter 6

CONCLUSIONS

Stable isotope compositions of water were measured at 13 sites along the South Platte River, with an additional 4 sampling sites at tributaries and reservoirs of this river system. Isotope compositions ranged from -110.2 ‰ to -94.5 ‰ δ^2H and from -14.4 ‰ to -12.0 ‰ $\delta^{18}O$, plotting (except two sampling points) below the Rocky Mountain Meteoric Water Line ($\delta^2H = 8.1\delta^{18}O + 14.8$ ‰). δ^2H and $\delta^{18}O$ compositions that plot below the Global Meteoric Water Line indicate these have been fractionated by evaporation, which occurs under non-equilibrium conditions. When evaporation occurred, the lighter isotope forms were transformed into the vapor phase causing a concentration or enrichment in the remaining water of the heavier isotope forms.

Enrichment in mean isotope compositions occurred with increasing distance downstream, from Henderson (SP1) (-110.2 ‰ δ^2H and -14.4 ‰ $\delta^{18}O$) to Julesburg (-94.5 ‰ δ^2H and -12.0 ‰ $\delta^{18}O$). Besides evaporation, enrichment in the river water occurred as enriched tributary and reservoir influx discharged into the South Platte. Overall, mean isotope compositions of the Big Thompson River (-110.0 ‰ δ^2H and -14.0 ‰ $\delta^{18}O$) and Cache la Poudre River (-110.1 ‰ δ^2H and -14.1 ‰ $\delta^{18}O$) were similar to those above the confluence with each (-109.5 to -109.0 ‰ δ^2H and -14.1to -14.0 ‰ $\delta^{18}O$). Mean isotope compositions at Riverside (-98.1 ‰ δ^2H and -12.1 ‰ $\delta^{18}O$) and Jackson Lake Reservoir (-79.3 ‰ δ^2H and -8.9 ‰ $\delta^{18}O$) were enriched relative to that above the confluence at Kersey (-109.4 ‰ δ^2H and -14.0 ‰ $\delta^{18}O$).

A change in mean isotope compositions was observed during different seasons. Mean isotope compositions in the fall of 2009 (-98.9 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$) and winter of 2009-2010 (-100.7 ‰ δ^2H and -12.5 ‰ $\delta^{18}O$) suggest there was a single water source predominating discharge in the river. The similarity of isotope compositions at Henderson (-110.2 ‰, -107.4 ‰ δ^2H and -14.1 ‰, -13.9 ‰ $\delta^{18}O$) during the winter and wastewater effluent samples (-110.5 ‰ and -107.9 ‰ δ^2H and -14.6 ‰ and -14.2 ‰ $\delta^{18}O$) suggest wastewater effluent mainly contributed flow during the fall and winter season, constituting the low flow period. During the spring of 2010 (-111.9 ‰ to -90.2 ‰ δ^2H and -17.1 ‰ to -12.5 ‰ $\delta^{18}O$), mean isotope compositions became depleted as snowmelt received from the Central Colorado Rocky Mountains contributed high discharge to the river.

Overall, during the low flow period, mean isotope compositions (-99.5 ‰ δ^2H and -12.8 ‰ $\delta^{18}O$) enriched relative to mean isotope compositions during the high flow period (-110.1 ‰ δ^2H and -14.3 ‰ $\delta^{18}O$). Discharge during the low flow period ranged from 120 to 8650 ft^3/s, while these ranged from 2800 and 8650 ft^3/s during the high flow period, as a result of high volumes being contributed by isotopically depleted snowmelt. During the high flow period, a significant depletion on mean isotope composition was observed at the Cache la Poudre River (-121.7 ‰ δ^2H), relative to that upstream at Evans (-114.7 ‰ δ^2H), indicating a change in isotope compositions between different flow periods.

Chapter 7

RECOMMENDATIONS

In order to characterize in more detail the isotope compositions along the South Platte River and their spatial, temporal and discharge variations, several suggestions are made below which could provide more information and improve the outcome of the study.

- More sampling sites along the river, specifically between Kersey and Weldona, would provide isotope signatures for this part of the river and would allow for more information on the effect reservoir water influx could have on river water.
- The collection of water samples on other reservoirs along the South Platte River (e.g., Prewitt Reservoir, Sterling Reservoir and Jumbo Reservoir).
- The collection of samples upstream of the urban area of Denver would provide information on the variation of isotope compositions between a forest environmental setting and the urban environmental setting as well as the effect the urban setting has on isotope compositions.
- The collection of more samples in the wastewater treatment plant in Denver and other treatment plants along the Front Range would provide a more clear characterization of stable isotope compositions in wastewater effluent.

- The characterization and temporal change in stable isotope compositions could be better if water samples were collected on a monthly basis.
- The collection of groundwater samples and the stable isotope characterization of these would help understand the role of irrigation return flow to the South Platte River.

Chapter 8

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